

# **STANDARD METHODS OF CHEMICAL ANALYSIS**

# STANDARD METHODS OF CHEMICAL ANALYSIS

SIXTH EDITION

*Volume Two—Industrial and Natural Products and  
Noninstrumental Methods*

Part A

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IN COLLABORATION WITH MANY CONTRIBUTORS  
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## PREFACE

Changes in the methods of chemical analysis, both major modifications and precise refinements, have been manifold during the twenty-five years since publication of the Fifth Edition of STANDARD METHODS OF CHEMICAL ANALYSIS. As a result of the development of new analytical techniques, as well as an expanding interest in the variety of materials subject to examination, analysis and analysts have recognized—and continue to stress—the necessity for comprehending the essential importance of substances considered insignificant only a few decades ago.

The preparation of a Sixth Edition of STANDARD METHODS OF CHEMICAL ANALYSIS was inevitable if the work were to maintain its utilitarian function in the onrush of contemporary change. Volume II, consequently, has undergone considerable expansion in content, evidenced by its physical size—approximately twice that of the Fifth Edition. Despite the changes in treatment and content, the purpose of this volume remains identical to that expressed in the First Edition. As an explanation of the aim of the present volume, we quote from the original Preface:

"This book is a compilation of carefully selected methods of technical analysis that have proven of practical value to the professional chemist. The subjects have been presented with sufficient detail to enable one with an elementary knowledge of analytical processes to follow the directions; on the other hand, lengthy exposition, theoretical dissertation, and experimental data are purposely avoided, in order to include a large amount of information in a compact, accessible form. References to original papers are given when deemed advisable."

The organization of the Sixth Edition is similar to that of the Fifth, but an extensive new part, *Apparatus, General Operations, and Reagents*, has been added. This consists of sixteen chapters, of which the following thirteen are new: *Standard Laboratory Apparatus; Detection of the Cations and Anions; Mechanical Separation; Separation by Precipitation; Separation by Electrolysis; Solvent Extraction; Separations by Distillation and Evaporation; Chromatography; Ion Exchange Methods in Analysis; Final Gravimetric Treatment; Acid-Base Titrations in Nonaqueous Solvents; Statistical Interpretations; and Quantitative Organic Analysis.*

In Part II, *Special Techniques for Industrial Products and Other Special Substances*, ten new chapters have been added: *Air Pollutants; Amino Acid Analysis of Protein Hydrolyzates; Chemical Analysis in Clinical Medicine; Fertilizers; Gas Analysis—Vacuum Techniques; Pesticides; Plastics; Silicates; Glasses, Rocks, and Ferrous Slags; Soils; and Vitamins.*

Almost without exception, chapters that appeared in the Fifth Edition have been completely rewritten. Of the fifty chapters appearing in this edition, only four have the same authors as previously. In those instances where chapters appearing in the Fifth Edition have been prepared for the Sixth Edition by different authors, they have been rewritten and not merely revised.

The editor has received much useful assistance from many sources, and wishes to express his gratitude here as well as later in the text. Special mention should be made of Professor N. Howell Furman, editor of the Fifth Edition, and Volume I of the Sixth Edition. As advisory editor of Volume II, he prepared the outline used in

organizing the text, gave valuable assistance in securing contributors for the many chapters, and made many helpful suggestions and criticisms.

The editor wishes to acknowledge also the valuable assistance given by Dean Virgil Hunt of the Indianapolis Regional Campus of Indiana University in making available the many facilities of his department to aid the completion of this book. Furthermore, a number of people have rendered invaluable aid in typing portions of the manuscript, attending to correspondence, proofreading, and preparing the Index. These are: Janet Boling, Patricia Van Noy, Oka Negley, Ruth Moody, and Judy Call.

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The task of assembling and coordinating the material for this book has been simplified immensely by the remarkable spirit of cooperation exhibited by the various collaborators in all phases of the undertaking. The editor wishes to thank all contributors for their efforts toward bringing this book to its final form, and for making available the specialized information that it contains to all who may have need of the methods of practical chemical analysis.

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*Part I*

**APPARATUS, GENERAL  
OPERATIONS, AND  
REAGENTS**

## Chapter 1

# STANDARD LABORATORY APPARATUS

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Quantitative analysis is the determination of the quantity of one or more of the constituents present in a given material. Regardless of the method used to determine this quantity, somewhere in the operation a set of precise analytical weights and an analytical balance must be used. Therefore, the accuracy of all work rests fundamentally on the weights and balance that are employed. H. S. Washington states ". . . if the balance and weights are not accurate, and are not carefully taken care of, the labor and time expended on an analysis will largely go for naught. The balance and weights should therefore be regarded with a feeling akin to reverence, and the balance case looked upon, so to speak, as a 'sanctum sanctorum'."

## WEIGHTS, BALANCES, AND WEIGHING

*The Weights.*—As is well known, the international metric system is used in scientific work, and the standard of mass is the international prototype kilogram which is in the custody of the International Bureau of Weights and Measures in France. Two copies of this standard, designated as the United States prototype kilograms, are at the National Bureau of Standards, Washington, D. C. These weights are the ultimate base for all gravimetric analysis.

The analyst should exercise extreme care in selecting the weights he uses. The material of which analytical weights are made must be hard, nonmagnetic, resistant to oxidization and corrosion, and unaffected by humidity. The entire surface of each weight must be smooth and highly polished, and must remain so in use. The weights must always be handled with the special lifter which the manufacturer provides with each set of weights. These lifters are especially designed, and the tips that come in contact with the weights must be smooth and made of a material that minimizes the abrasion of the weights during use. Nonmagnetic stainless steel is suitable for weights of 1 g. and larger. Platinum or an alloy of 96.5% platinum and 3.5% rhodium is suitable for fractional gram weights of 10 mg. or larger. Highly polished tantalum is suitable for the fractional gram weights of less than 10 mg.

The accuracy of a set of weights should never be taken for granted. This is

true for a new set, as well as for a set that has been used. There are extreme variations in the quality of weights, and nothing except a test of each individual weight will prove its accuracy and constancy. It would be ideal if every set of weights that is used in analytical work were tested by the National Bureau of Standards,<sup>1</sup> but this may not be practical. Therefore, every first class laboratory should have available a set of weights certified by the National Bureau of Standards as conforming to Class M weights. These weights then can be used to determine the accuracy of the normal "working" weights. For weights to conform to Class M or Class S, they must be adjusted within the limits of error prescribed in Table I-1.

The mere fact that a set of calibrated weights is not available is no excuse for an analyst to use questionable weights. Inaccurate weights often go undiscovered, either through ignorance or through fear that the calibration methods are too difficult or too time-consuming to be practicable in an ordinary analytical laboratory. A quick check for gross inaccuracies can be made by a few simple weighings. Since most gravimetric analyses are reported as ratios or percentages, it is usually sufficient that the set of weights used be nearly consistent among themselves, that is, the 1-g. weight be exactly 10 times the weight of the 100 milligram weight and the 10-g. weight be exactly 10 times the weight of the 1-g. weight. The method of calibration that can be used is that of Richards<sup>2</sup> in which one weight, perhaps the 10-g., is assumed correct; that is, it weighs 10.0000 g. The values of all other weights can be expressed in terms of this 10-g. weight.

**The Analytical Balance.**—The value of gravimetric analysis rests fundamentally on the accuracy of the instrument employed to determine the weight of the sample to be analyzed as well as to determine the weights of the various component parts. The instrument used is the analytical balance, which is the oldest form of instrument in use in analytical chemistry. The analytical balance is used to compare the weight of the sample to be analyzed to the standard unit of weight (mass), and likewise to compare the weights of the various separated components to the same standard unit of weight.

The fundamental requirements for a reliable analytical balance are:

A. It must be accurate and precise. It should give the same results when the same object is weighed several times.

B. It must have sufficient sensitivity. It must respond to slight changes in weight. For most analyses it is sufficiently sensitive if one can easily determine 0.1 mg.

C. Above all, the balance must be stable and well constructed. The beam must return to its horizontal position after swinging. The beam must not bend under its normal working load. All knife-edges must be sharp, lie in the same plane, and be parallel to one another. The plates on which the knife-edges rest when weighing should be made of a hard material, usually agate, highly polished, and perfectly smooth and flat. The knife-edges should remain sharp and the plates flat, "not cupped," when the balance is properly used.

There are three general types of analytical balances available to the analyst. One type of analytical balance is essentially an equal-armed lever, supported at the center and free to swing in a vertical plane. Balance pans are suspended from

<sup>1</sup> Schedules of fees charged by the National Bureau of Standards for the testing of weights and balances, methods of weighing and testing, and regulations governing their testing may be obtained free of charge from the National Bureau of Standards, Washington 25, D. C.

<sup>2</sup> Richards, T. W., *J. Am. Chem. Soc.*, 22, 144, 1900.

TABLE 1-1. PRECISION OF CORRECTIONS AND TOLERANCES FOR CLASS M, HIGH PRECISION WEIGHTS, AND CLASS S, LABORATORY WEIGHTS

Denomination	Class M		Class S	
	Tolerance	Precision of Correction	Tolerance	Precision of Correction
100 g.	0.5 mg.	0.1 mg.	0.5 mg.	0.5 mg.
50	.3	.1	.3	0.1
20	.2	.01	.2	.1
10	.15	.01	.15	.05
5	.15	.01	.15	.05
2	.10	.01	.10	.05
1	.10	.01	.10	.05
500 mg.	.05	.001	.05	.01
200	.05	.001	.05	.01
100	.05	.001	.05	.01
50	.03	.001	.03	.01
20	.03	.001	.03	.01
10	.02	.001	.02	.01
5	.02	.001	.02	.01
2	.01	.001	.01	.01
1	.01	.001	.01	.01
0.5	.01	.001	.01	.01
0.2	.01	.001	.01	.01
0.1	.01	.001	.01	.01

each end of the beam or lever. The object to be weighed and the weights used are placed on these pans. Analytical balance of this type may differ in various constructional details, but all have the same fundamental features. The final weight is obtained by one of the methods of swings. A second type of analytical balance is constructed exactly like the previous type except that some kind of damper, usually of a magnetic type, is attached to one or both ends of the beam. The purpose of the damper is to eliminate the swinging of the balance. In fact, the oscillations are so completely damped that, if there is a small difference in the weights on the pans and the balance is released, the pointer will swing to one side and come to rest at the end of its swing. The scale is graduated in milligrams; thus, the point of rest indicates directly the weight of the object. Naturally, the exact point of rest must be determined either with a microscope, or the two images, pointer and scale, are magnified and projected on some type of viewing screen.

A third type of analytical balance may or may not be an equal-arm balance. In either case, it is a so-called damped balance. This type of balance may be called a one-pan balance. That is to say, attached to the beam on one side of the fulcrum is a counterpoise of sufficient weight to balance exactly the pan and

weights on the opposite side. The total load on the balance is always constant and weighing is made by substitution; that is, with the unknown on the pan of the balance, weights are removed from the pan side of the beam until the equilibrium is restored. Thus, the amount of weight removed is the weight of the unknown object. The balance has its own set of built-in weights which are removed from, or placed on, the pan side by means of some type of levers. These weights normally hang from the weight hanger which is attached to the stirrup. Lashof and Macurdy have published a method for checking this type of balance and weights.<sup>3</sup>

Each type of analytical balance may be obtained with at least three different capacities; namely, a normal analytical balance of 200-g. capacity, a semi-micro of 50- to 100-g. capacity, and a micro of 20-g. capacity.

Regardless of the type of analytical balance used, it must be placed on a firm foundation and protected as much as possible from vibrations and jarring. It should also be protected from changes in temperature, and never placed near a window, an air conditioner, or a radiator, or other source of heat (including incandescent light). Above all, it should not be placed in a laboratory where it can be subjected to various corroding gases.

**The Weighing.**—The fact that an analyst has an excellent set of calibrated weights and uses an excellent balance is not positive proof that the weighings are correct. To obtain true and exact weights, much depends on the technique used in the manipulation of the balance and the weights and the objects being weighed.

The balance beam should always be raised or lowered with extreme caution; this prevents undue damage both to the knife-edges and the planes on which they operate. The weights and the object being weighed must always be placed in the center of the pan. Weights should always be handled with forceps and never with the fingers. Weights of the highest accuracy should be kept in a closed box when not in use. However, those weights that are in continuous use for ordinary work can be kept in a suitable place within the balance case, provided the case is reasonably tight and the balance door is kept shut when not in use.

Objects to be weighed must, of course, be allowed to come to the same temperature as the balance before weighing is attempted. The time required for the temperature of any object to come to the same temperature of the balance will depend on the size and kind of material, as well as on the temperature at which it was dried or ignited. For instance, if several porcelain crucibles are removed from a furnace at a temperature of 900°C. and placed in a desiccator, there is sufficient heat present to warm up the entire desiccator and many hours are required for the desiccator and the crucibles to come to the same temperature as the balance. In a case like this, it is best to allow the desiccator to remain on a laboratory bench for several hours to dissipate as much heat as possible. Then allow the desiccator to stand near the balance for at least over night before attempting any weighings.

Many objects, especially if they are made of glass or quartz, become electrified by friction. This electrification is caused by wiping or rubbing; therefore, such objects should not be wiped immediately before weighing. Electrification may also be caused by undue sliding of the object along the base on which it rests, as well as by twisting of the ground glass stopper or cap of a weighing bottle. The presence of a static electrical charge on an object being weighed causes erratic behavior of the balance. If the method of swings is used with an equal-arm bal-

<sup>3</sup> Lashof, T. W., and Macurdy, L. B., *Anal. Chem.*, 26, 707, 1954.



ance, the swings are erratic. Likewise, the weight obtained by a damped balance may vary by plus or minus several tenths of a milligram on successive trials. This effect is due to the attraction or repulsion of the charged container for the wall or floor of the balance. This static electrical charge can be very annoying, especially when the relative humidity is low. It is reported that the charge may be dissipated by placing a small amount of radioactive material in the balance case to ionize the air. The use of a "high-frequency vacuum tester" for the removal of the electrostatic charge has been recommended by Van Straten and Ehret.<sup>4</sup> The best method available is to handle the object to be weighed in such a manner that it does not become electrified.

Another source of error is the adsorption of moisture. It is a known fact that any perfectly dry object placed in a moist atmosphere will adsorb moisture on its surface. The amount of moisture, which causes an increase in weight, will depend primarily on the properties of the material itself and on the relative humidity of the atmosphere to which it is exposed.

Materials like platinum, nickel, and most porcelain, which are used to make crucibles and dishes, are so very slightly hygroscopic that, when properly heated and cooled, they will not adsorb sufficient moisture to cause an increase in weight in the time required to make the weighing. Other materials like glass, quartz, etc., especially if they have a large surface, may increase considerably in weight due to moisture adsorbed during the time of weighing. The errors due to adsorption of moisture on the surfaces of containers can be minimized by the use of a tare. Such a tare is a similar container, both in weight and surface, and is exposed to the same cleaning, drying, and cooling as the container in which the object to be weighed was exposed.

One of the principal sources of error is the absorption of moisture by the substance being weighed, which is usually of much larger magnitude than the adsorption by the container. The amount of moisture absorbed will depend on the nature of the substance. Materials like anhydrous aluminum chloride and phosphorus pentoxide and similar substances absorb water very rapidly and must be weighed in tightly closed containers. Materials like sodium chloride, ammonium dihydrogen phosphate, and metal chips may be weighed in open containers. Naturally, there are materials between these two extremes so that the precaution to take while weighing will depend on the particular substance being weighed. The physical characteristics of a substance must also be considered: silica gel is so hygroscopic that it may be used as a desiccant and must therefore be weighed in a closed container, whereas pieces of quartz may be weighed in open containers. Likewise, zirconium oxide that has been formed by ignition at 600°C. is so hygroscopic that it must be weighed in a closed container; yet, if the same material is heated at 900° to 1000°C., it may be weighed in open crucibles. There are many other substances that have similar characteristics. Therefore, to make accurate weighings one must know something about the nature and history of the object to be weighed.

A body that is weighed in air is buoyed up by a force equivalent to the weight of the volume of air displaced by the body. This buoyancy effect must be taken into account and corrected for in analytical work of the most precise nature, such as the intercomparison of standard substances, the determination of the accuracy of a method, the standardization of acids or alkalis, and especially in the deter-

<sup>4</sup> Van Straten, F. W., and Ehret, W. F., *Ind. Eng. Chem., Anal. Ed.*, 9, 443, 1937.

mination of atomic weights. For most analytical work it is sufficient to use the weight obtained with stainless steel weight in air under normal conditions. If necessary, the weight of an object in vacuum may be calculated from the weight in air by the following equation:

$$M = W_A + \rho \left( \frac{W_A}{D_1} - \frac{W_A}{D_2} \right)$$

where  $M$  is the weight in vacuum,  $W_A$ , apparent weight in air,  $\rho$ , density of air,  $D_1$ , density of object, and  $D_2$ , density of weights.

## VOLUMETRIC APPARATUS

The value of volumetric analysis rests, as in gravimetric analysis, fundamentally on the accuracy of the instruments employed to determine the volume of a standard solution required to react with a known quantity of an unknown substance. This applies also to the measurement of an aliquot of the solution of the sample to be analyzed. The instruments used are volumetric flasks, burets, transfer pipets, and measuring pipets. They are made in various sizes.

**Volumetric Units.**—The fundamental unit of capacity is the liter. A liter is the volume occupied by one kilogram of water at its maximum density (3.98°C.) and under normal atmospheric pressure (760 mm. of mercury pressure). The volume is measured under normal atmospheric pressure, but the mass, one kilogram of the water, is the weight in vacuum. In volumetric analysis the unit most used is the milliliter (ml.), which is one one-thousandth of the liter. The unit milliliter (ml.) should not be confused with the unit cubic centimeter (cc.). The cubic centimeter is a unit of volume derived from the meter, which is the standard for length. It was originally intended that 1 ml. of water be exactly equivalent to 1 cc. of water and each have a mass of 1 g. when the water was at its maximum density (3.98°C.). Extensive investigation by the International Bureau of Weights and Measures<sup>5</sup> revealed that 1 ml. is equal to 1.000028 cc. Actually this small difference has no significance in ordinary volumetric analysis, but to be correct the unit milliliter should be used instead of the unit cubic centimeter.

**Labeling of Glassware.**—Every item of volumetric apparatus should bear the following information inscribed in permanent legible characters, either by etching, or by fused markings provided the latter are neat and clear.

1. The capacity of the apparatus.
2. The temperature at which it is calibrated.
3. Method of use; that is, to contain or deliver.
4. The name or trade-mark of the maker.
5. A permanent identification number. If there are detachable parts, such as stoppers, stopcocks, etc., they must be marked with the same number unless they are interchangeable standard taper. If there are interchangeable ground-glass parts, both parts must be marked with the proper standard taper symbol.
6. The time required to deliver the stated volume, with unrestricted outflow, if the apparatus is designed to deliver a definite volume through an orifice.
7. Type of glass; that is, soft glass or a borosilicate glass.

<sup>5</sup> Ch. Ed. Gillaume, *La Creation du Bureau International des Poids et Mesures et son Oeuvre*, Paris, 1927, p. 258.

**Reading of Meniscus.**—The use of all volumetric ware requires the setting or reading of a meniscus, and to do this accurately is more difficult than most analysts realize. The reading or setting is made on the lowest point of the meniscus, except for those liquids that are so strongly colored that they are opaque. One source of error is the determination of the exact bottom of the meniscus. This task is made difficult by reflections from the glass surface and the curved surface of the meniscus itself. A second source of error is parallax. These two errors can be minimized by the use of a reading aid. The simplest, and perhaps the best, reading device is a partial ring cut from a rubber stopper. The top part of a No. 3 or 5 rubber stopper is cut so that it is about 0.5 cm. thick. A hole, having a diameter slightly less than the diameter of a buret, is cut through this rubber disk, and a small segment is cut from this rubber ring. The reading device is placed one graduation below the meniscus and a white card is held behind the buret at the same point. The white card cuts out all reflections and the black rubber ring shades the bottom of the meniscus, thus making it appear as a curved line. The proper setting of the liquid level in a buret is to have the bottom of the graduation line on the front of the buret, the bottom of the meniscus as defined with the reading device described, and the top of the graduation line on the back of the buret all in one plane. Similar reading aids can be made to fit the stems of pipets and the necks of flasks. A third source of error, only present in apparatus designed to deliver, is drainage. The error due to drainage is fairly independent of temperature over the normal range of temperature encountered in volumetric analysis. The amount of liquid remaining on the wall of a container is directly proportional to the area of the wall. Therefore, the smaller the diameter the larger is the ratio between the amount remaining and the quantity delivered. The drainage and the amount adhering to the wall are inversely proportional to the time allowed for delivery. This error can be minimized by using the same buret and regulating the time required to titrate an unknown to within narrow limits to the time required to titrate the standard solution.

**Quality of Glassware.**—All volumetric apparatus must be of high quality; that is, it should be well constructed and free from striae and surface irregularities. The cross section where the setting is made or the meniscus is read must be circular. The shape of the apparatus must permit thorough cleaning and complete emptying and drainage. The transition from larger to smaller diameters must be gradual and regular and contain no sharp ledge or shoulder to entrap either liquids or gases. All ground glass stopcocks or stoppers, and plastic stopcocks or stoppers, must be fitted so as to work easily and prevent leakage.

Volumetric apparatus of excellent quality can be purchased. If desired, apparatus certified by the National Bureau of Standards can be purchased through most laboratory supply companies, or one can send their apparatus directly to the National Bureau of Standards for certification.<sup>6</sup> However, it is desirable that the analytical chemist test the correctness of his volumetric apparatus and thus become familiar with its limitations.

**Criterion of Cleanliness of Glassware.**—The apparatus must be clean, and for general analysis the surface may be considered clean if, after rinsing several times (minimum of 5) with distilled water, the water will drain off freely and uniformly without leaving any dry streaks or drops of water on the walls. In the special

<sup>6</sup> See Testing of Glass Volumetric Apparatus, National Bureau of Standards Circular 602, 1959.

case where "trace" amounts of elements are involved, some other special criteria for a clean surface may be required.

**Calibration.**—Burets and measuring pipets should be checked at a minimum of five points. For a 50-ml. buret the intervals 0–10 ml., 0–20 ml., 0–30 ml., 0–40 ml., and 0–50 ml. should be checked. To do this, fill the buret to just above the zero line with distilled water at room temperature and determine the temperature,  $T$ , of the water. Set the meniscus at exactly zero, as previously described, and wipe off the excess water from the tip with a clean piece of filter paper. Place a tared stoppered flask under the buret and deliver the interval to be tested into the tared stoppered flask and reweigh the flask. The true volume of the interval is calculated from the apparent weight of the water at temperature  $T$  by means of Table 1-2 or Table 1-3, depending on the type of glass from which the buret or pipet is made. Tables 1-2 and 1-3 correspond to Tables 16 and 17 published in

TABLE 1-2. CORRECTIONS FOR DETERMINING THE TRUE CAPACITIES OF GLASS VESSELS FROM THE WEIGHT OF WATER IN AIR

(Soft glass, coefficient of cubical expansion 0.000025/°C.)

Indicated capacity 100 ml.

Temperature, °C.	Tenths of degrees									
	0	1	2	3	4	5	6	7	8	9
15	0.207	0.208	0.210	0.211	0.212	0.213	0.215	0.216	0.217	0.219
16	.220	.221	.223	.224	.225	.227	.228	.230	.231	.232
17	.234	.235	.237	.238	.240	.241	.243	.244	.246	.247
18	.249	.250	.252	.253	.255	.257	.258	.260	.261	.263
19	.265	.266	.268	.270	.272	.273	.275	.277	.278	.280
20	.282	.284	.285	.287	.289	.291	.293	.294	.296	.298
21	.300	.302	.304	.306	.308	.310	.312	.314	.315	.317
22	.319	.321	.323	.325	.327	.329	.331	.333	.336	.338
23	.340	.342	.344	.346	.348	.350	.352	.354	.357	.359
24	.361	.363	.365	.368	.370	.372	.374	.376	.379	.381
25	.383	.386	.388	.390	.392	.395	.397	.399	.402	.404
26	.406	.409	.411	.414	.416	.418	.421	.423	.426	.428
27	.431	.433	.436	.438	.440	.443	.446	.448	.451	.453
28	.456	.458	.461	.463	.466	.469	.471	.474	.476	.479
29	.482	.484	.487	.490	.492	.495	.498	.501	.503	.506
30	.509	.511	.514	.517	.520	.522	.525	.528	.531	.534
31	.536	.539	.542	.545	.548	.551	.554	.556	.559	.562
32	.565	.568	.571	.574	.577	.580	.583	.586	.589	.592

TABLE 1-3. CORRECTIONS FOR DETERMINING THE TRUE CAPACITIES OF GLASS VESSELS FROM THE WEIGHT OF WATER IN AIR

(Borosilicate glass, coefficient of cubical expansion 0.000010/°C.)

Indicated capacity 100 ml.

Temperature, °C.	Tenths of degrees									
	0	1	2	3	4	5	6	7	8	9
15	0.200	0.201	0.202	0.204	0.205	0.207	0.208	0.210	0.211	0.212
16	.214	.215	.217	.218	.220	.222	.223	.225	.226	.228
17	.229	.231	.232	.234	.236	.237	.239	.241	.242	.244
18	.246	.247	.249	.251	.253	.254	.256	.258	.260	.261
19	.263	.265	.267	.269	.271	.272	.274	.276	.278	.280
20	.282	.284	.286	.288	.290	.292	.294	.296	.298	.300
21	.302	.304	.306	.308	.310	.312	.314	.316	.318	.320
22	.322	.324	.327	.329	.331	.333	.335	.338	.340	.342
23	.344	.346	.349	.351	.353	.355	.358	.360	.362	.365
24	.367	.369	.372	.374	.376	.379	.381	.383	.386	.388
25	.391	.393	.396	.398	.400	.403	.405	.408	.410	.413
26	.415	.418	.420	.423	.426	.428	.431	.433	.436	.438
27	.441	.444	.446	.449	.452	.454	.457	.460	.462	.465
28	.468	.470	.473	.476	.479	.481	.484	.487	.490	.492
29	.495	.498	.501	.504	.506	.509	.512	.515	.518	.521
30	.524	.526	.529	.532	.535	.538	.541	.544	.547	.550
31	.553	.556	.559	.562	.565	.568	.571	.574	.577	.580
32	.583	.586	.589	.592	.595	.598	.602	.605	.608	.611

the NBS Circular 602. For the 40.00-ml. interval, determined at 26.4°C., the calculation would be:

Apparent weight of water	39.839 g.
From Table 1-2, $0.4 \times 0.416$	0.166
True volume at 20°C.	40.004 ml.

All observations must be made in duplicates and the duplicates should agree to within  $\frac{1}{4}$  of the limit of error for that particular size of apparatus, as recommended by the National Bureau of Standards. Duplicate observations on a 50-ml. buret should agree to within 0.007 ml.; on a 10-ml. buret to within 0.003 ml. The limits of error permitted are shown in Tables 1-4 and 1-5.

TABLE 1-4. CAPACITY TOLERANCES FOR BURETS AND MEASURING PIPETS

Capacity (in milliliters) of total graduated portion less than and including—	Limit of error of total or partial capacity	
	Burets	Measuring pipets
	ml.	ml.
2	...	0.01
5	0.01	.02
10	.02	.03
30	.03	.05
50	.05	.08
100	.10	.15

The calibration of transfer pipets is also checked by determining the apparent weight of water delivered and making the appropriate correction. The limit of errors for transfer pipets is shown in Table 1-5. The pipet is filled to just above the mark, the upper end is closed, normally with the index finger which should be slightly moistened; and the outside of the tip is wiped dry with a piece of clean filter paper. The meniscus of the liquid is adjusted to the mark by careful admittance of air. The pipet tip is then rested against the inside wall of a receiving vessel and the contents delivered, with free outflow. A more precise method of using a transfer pipet is to attach a short piece, about 10 to 15 cm., of clean rubber tubing to the upper end of the pipet and then close this tubing with a screw clamp or a pinch cock. The inside diameter of the rubber tubing

TABLE 1-5 CAPACITY TOLERANCES FOR TRANSFER PIPETS

Capacity (in milliliters) less than and including—	Limit of error
	ml.
2	0.006
5	.01
10	.02
30	.03
50	.05
100	.08
200	.10

should be slightly less than the outside diameter of the upper stem of the pipet and the clamp placed about 1 or 2 cm. from the top end of the pipet. The pipet is filled to just above the mark, as usual, and the clamp closed. The pipet is then placed in a buret clamp and thus held rigid. The tip is wiped dry and the meniscus adjusted to the mark by gently and carefully pushing the rubber tube further on to the pipet stem. Any excess liquid is removed from the tip with a piece of clean filter paper. The receiving vessel is then placed under the pipet, with the tip of the pipet touching the inside wall. Then the clamp is loosened and the liquid allowed to deliver under free flow. The latter method eliminates any chance of accidentally losing a drop of liquid from the end of the pipet while it is being transported to the receiving vessel.

To check the capacity of flasks that are calibrated to contain a definite volume, clean, dry, and tare the flask. Fill the flask to the mark with distilled water. Determine the temperature and apparent weight of the water and calculate the volume by applying the appropriate correction from either Table 1-2 or Table 1-3.

**Weight Burets.**—Many special devices have been recommended from time to time that are supposed to eliminate the errors of drainage, parallax, changes in volume due to changes in temperature, etc. However, if a higher accuracy is desired than is obtainable when normal volumetric apparatus is used in its normal fashion, one should use weight burets. Weight burets are especially recommended since one has so many good rapid-weighing balances available. In titrations involving 50 ml., weighing to an accuracy of 1 mg. (1 part in 50,000) is quick and simple, whereas the determination of 50 ml. with a buret to 0.01 ml. (1 part in 5,000) is most difficult.

#### Advantages of Weight Burets.—

1. Standard solutions are made up on a weight basis (grams of standard substance per gram of solution) and all results are independent of temperature.

2. Frequent cleaning of the buret is not necessary because a drop of solution clinging to the inside wall of the weight buret does not affect the results.

3. Errors due to drainage are completely eliminated; in fact, with the modern quick weighing balances the weight buret can be weighed in the time normally allowed for an ordinary buret or pipet to drain.

## MISCELLANEOUS APPARATUS

There are several types of apparatus that should not, in a strict definition of standard, be called standard apparatus. The use of this apparatus is so important, however, that an analyst must know the composition and limitations of such apparatus before he can obtain reliable results when it is used. The analyst of the present day can select apparatus made from various materials, such as borosilicate glass, alkali-resistant glass, low actinic glass, platinum, gold, silver, nickel, stainless steel, iron, and many types of plastics.

The quality of apparatus has improved very much in recent years, but the discriminating analyst must still exercise caution in the selection of apparatus for particular analyses. Extreme care must be used in selecting apparatus, if one is determining "trace quantities (10  $\mu$ g. or less)" of an element.

## LABORATORY GLASSWARE

**Types of Glassware.**—All glassware that is used should be of the so-called resistant variety, and even this glassware is attacked by the solutions. The amount of at-

tack depends on the time, the temperature, the salt concentration, and whether the solutions are acid or alkaline. The chemical composition of four brands of chemical glassware available is given in Table 1-6. The chemical resistance of

TABLE 1-6. COMPOSITION OF THE SAMPLES

Constituent	Glasbake, Per Cent	Kimble, Per Cent	Pyrex Per Cent	Vycor, <sup>d</sup> Per Cent
SiO <sub>2</sub>	78.4	74.7	81.0	96.3
B <sub>2</sub> O <sub>3</sub>	14.0	9.6	13.0	2.9
R <sub>2</sub> O <sub>3</sub> <sup>a</sup>	2.5	5.6	2.2	0.4
ZnO	n. d. <sup>c</sup>	0.1	n. d.	n. d.
CaO	0.1	.9	neg. <sup>b</sup>	neg.
BaO	n. d.	2.2	n. d.	n. d.
MgO	neg.	neg.	n. d.	n. d.
Na <sub>2</sub> O	5.0	6.4	3.6	<0.02
K <sub>2</sub> O	neg.	0.5	0.2	<.02
As <sub>2</sub> O <sub>3</sub>	0.037	.027	.002	.005
Sb <sub>2</sub> O <sub>3</sub>	.038	.009	n. d.	n. d.

<sup>a</sup> Chiefly Al<sub>2</sub>O<sub>3</sub>.

<sup>b</sup> "neg." indicates a negligible amount of the constituent.

<sup>c</sup> "n. d." indicates the corresponding constituent was not detected.

<sup>d</sup> 0.3 per cent of undetermined constituents.

each is given in Fig. 1-1, 1-2, and 1-3, which show graphically the average loss in weight in milligrams sustained when 200 ml. of the selected solution were placed in 250-ml. Erlenmeyer flasks and boiled continuously for 6 hours on an electric hot plate.

For more detailed information, see Chemical Resistance of Laboratory Glass Ware, by Wichers, Finn, and Clabaugh.<sup>7</sup> Data is not available for the several types of laboratory glassware that have appeared on the market since 1941, but this latter ware should be used with caution.

## FILTERING CRUCIBLES

Filtering crucibles of various sizes and shapes are available. The crucibles are fabricated of glass, quartz, porcelain, stainless steel, and platinum. The filtering diaphragm of each is composed of the same material as the body of the crucible and is fabricated in place as an integral part of the crucible.

**Sintered-Glass Filtering Crucibles.**—The filtering diaphragm in the bottom of sintered-glass crucibles is made of glass particles that have been ground or powdered and sieved to produce particles of selected uniform size, and then sintered together to form a filtering mat of the desired porosity. They can be used to filter solutions that are neutral or acidic, and even concentrated acids. Naturally, solutions containing hydrofluoric acid will attack these sintered-glass crucibles, so

<sup>7</sup> Wichers, E., Finn, A. N., and Clabaugh, W. S., *J. Research NBS*, 26, 537, 1941; *Ind. Eng. Chem., Anal. Ed.*, 13, 419, 1941.



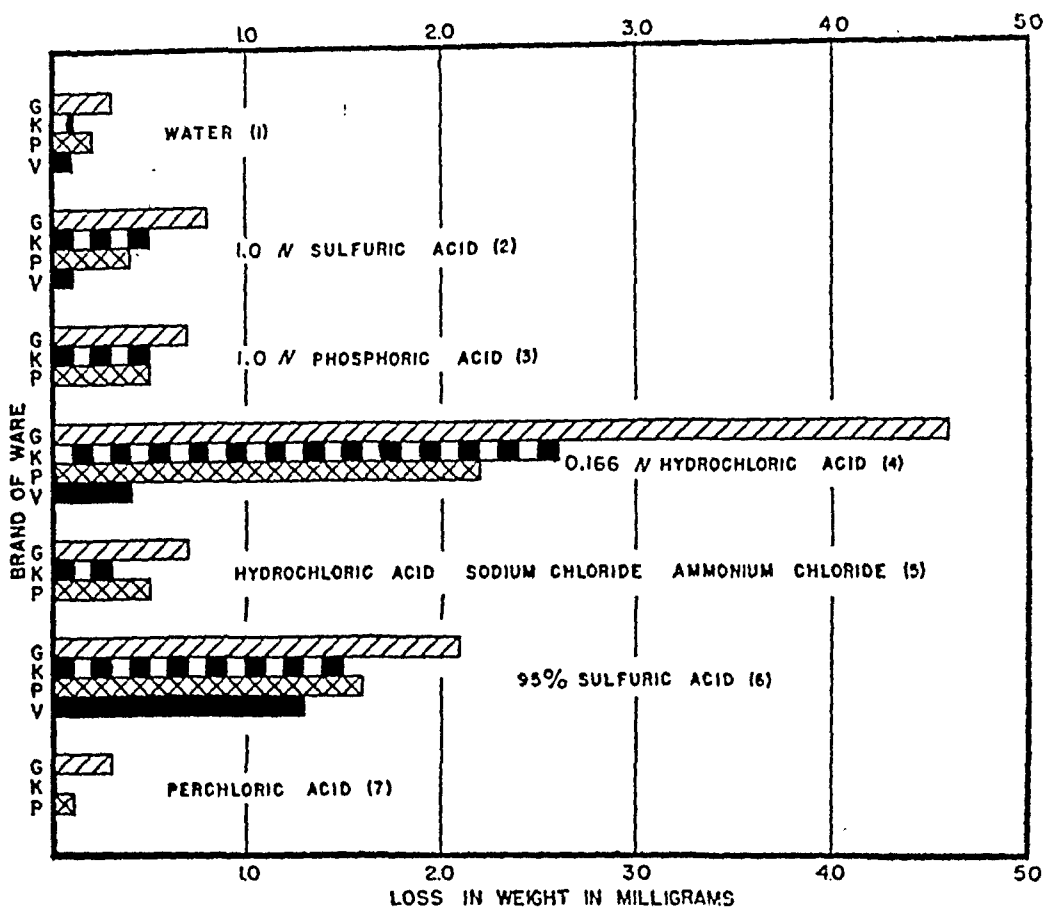


FIG. 1-1. Comparative Resistance to Acid Reagents and Water.

Average loss in weight, in milligrams, per flask per 6-hour period of exposure.

The numbers of the following explanatory notes correspond to the numbers attached to each group of data in Fig. 1-1.

- (1) Distilled water.
- (2) Approximately normal sulfuric acid.
- (3) Approximately normal phosphoric acid (one-third molar).
- (4) Approximately 6 N ("constant-boiling") hydrochloric acid. About midway of the 6-hour period of boiling, the flasks were replenished with acid of the same strength instead of with water.
- (5) A solution containing 50 ml. of concentrated hydrochloric acid, 50 g. of sodium chloride, and 50 g. of ammonium chloride, in 1 liter.
- (6) Sulfuric acid, 95 per cent. Fifty ml. was used instead of the usual 200 ml., and the flasks were heated on a gas hot plate. Since the area of glass exposed to the boiling acid was not the same as with most of the other reagents, the results are not directly comparable with those obtained with the others. No replenishment of acid was necessary.
- (7) Perchloric acid. Fifty ml. of 60% acid was used for the first period of 6 hours. The electric hot plate used did not supply enough heat to keep the acid boiling, but much of the acid evaporated. For the second period, 100 ml. of acid was used. The flasks were heated on a gas hot plate to keep the acid boiling gently. No acid was added during either of the 6-hour periods.

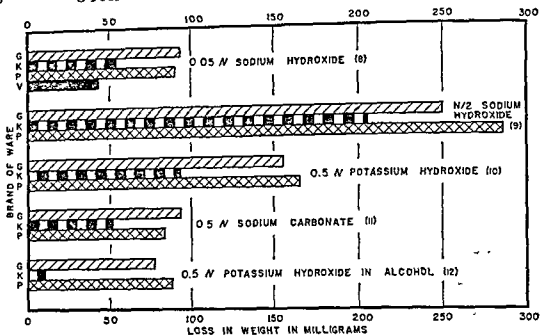


FIG. 1-2. Comparative Resistance to Alkaline Reagents.

Average loss in weight, in milligrams, per flask per 6-hour period of exposure.

For 0.5 N potassium hydroxide in alcohol the loss in weight shown is six times the average hourly loss reported in Table 15.

The numbers of the following explanatory notes correspond to the numbers attached to each group of data in Fig. 1-2.

(8) Twentieth-normal sodium hydroxide.

(9) Half-normal sodium hydroxide.

(10) Half-normal potassium hydroxide.

(11) Half-normal sodium carbonate.

(12) Half-normal potassium hydroxide in 95% alcohol. When this solution was used, the flasks were connected with water cooled reflux condensers, by means of rubber stoppers. The first period was 1 hour and the second 2 hours, instead of the usual two 6-hour periods. The object of this departure from the usual procedure was to simulate actual conditions under which alcoholic potash solutions are frequently used.

they should not be used for filtering such solutions. Likewise, alkaline solutions attack sintered-glass crucibles. Such a crucible may lose several tenths of a milligram in weight when 100 ml. of a solution having a pH of 8 is poured through it. If the pH of the solution is 10 to 12, the loss in weight may be as much as several milligrams. The porosity of the filter may change during use, due to the accumulation of silicic acid that is present in all solutions handled in glassware. This silicic acid clogs the pores, causing the filter to become more retentive and slower filtering. Since alkaline solutions tend to dissolve the glass, their continued use will increase the size of the pores and make the filter less retentive and faster filtering. Therefore, sintered-glass filtering crucibles that are in constant use should be checked to determine their suitability for retaining desired precipitates.

*Sintered-quartz filtering crucibles* are similar to sintered-glass filtering crucibles but are made entirely of clear quartz. Their main advantage is that they can be ignited at temperatures up to 1100°C. to 1200°C.

*Porous porcelain filtering crucibles* are similar to sintered-glass filtering crucibles but are made entirely of porcelain. They are more resistant to attack by alkaline solutions and may be ignited to 1000°C.-1200°C.

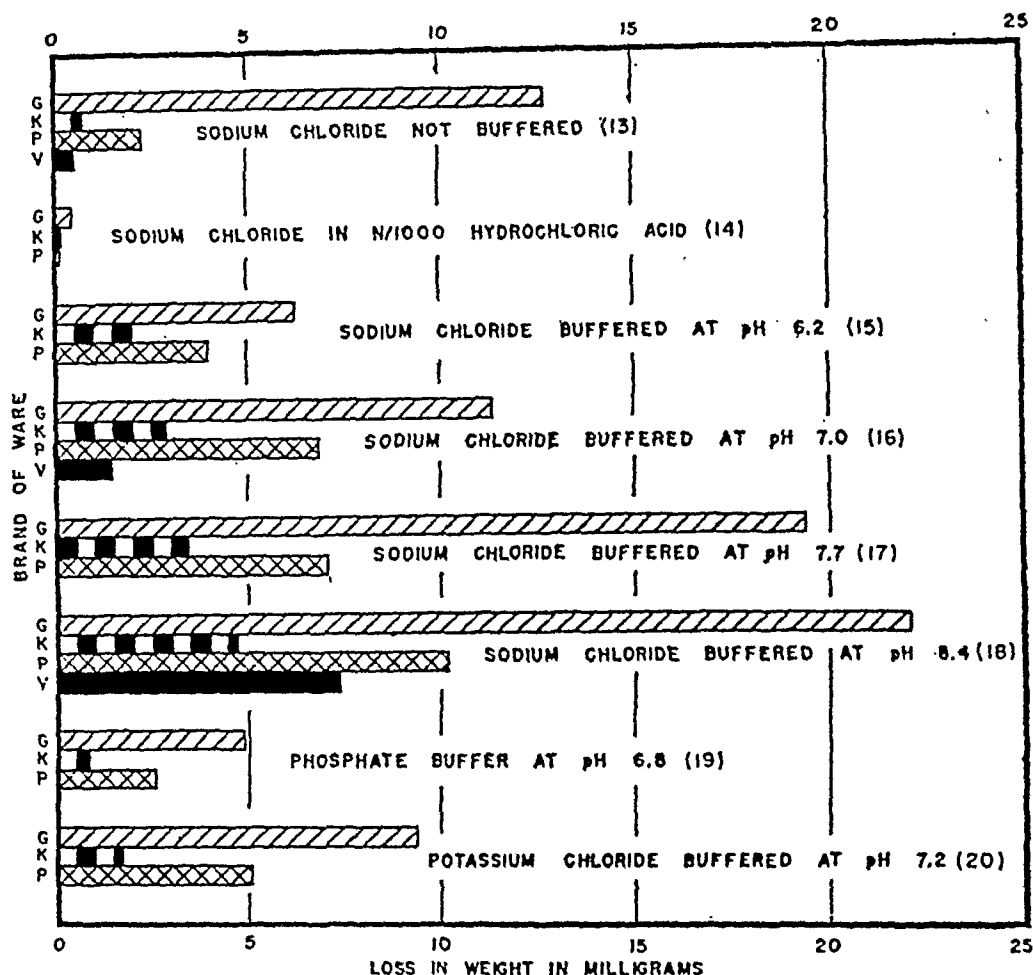


FIG. 1-3. Comparative Resistance to Nearly Neutral Reagents.

Average loss in weight, in milligrams, per flask per 6-hour period of exposure.

This group of reagents was made up chiefly of 5% solutions of sodium chloride (actually 50 g. of NaCl in 1 liter of solution) adjusted to selected points on the pH scale by means of mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate. The effect of nearly neutral salt solutions was studied in some detail after it was observed that an unbuffered 5% solution of sodium chloride caused a pronounced attack of all the glasses (although in varying degrees). The indicated pH is that of the solution at the beginning of the test period, at room temperature. The approximately neutral solutions used were as follows. The numbers of the paragraphs correspond to the numbers attached to the several groups of data in Fig. 1-3.

(13) Sodium chloride, 5%, not buffered. The solution was slightly acid at the beginning of the test period, but the contents of the flasks were slightly alkaline at the end of the period, especially in the group which showed the greatest attack.

(14) Sodium chloride, 5%, in 0.001 *N* hydrochloric acid. All the flasks were so slightly attacked by this reagent that they were used again with the next one. This is the only instance in which any flasks were used for tests with more than one reagent.

(15) Sodium chloride, 5%, buffered at pH 6.2. This solution contained, in addition to the sodium chloride, 10.85 g. of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and 4.55 g. of  $\text{KH}_2\text{PO}_4$ , in 1 liter.

(16) Sodium chloride, 5%, buffered at pH 7.0. In addition to the sodium chloride, the solution contained 19.0 g. of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and 1.15 g. of  $\text{KH}_2\text{PO}_4$ , in 1 liter.

(17) Sodium chloride, 5%, buffered at pH 7.7. The buffer salt concentrations were 33 g. of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and 0.25 g. of  $\text{KH}_2\text{PO}_4$ , in 1 liter.

(18) Sodium chloride, 5%, buffered at pH 8.4. The buffer salt concentration was 33 g. of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , in 1 liter.

(Caption continued on next page)

1250°C. Furnaces with the type of controls that regulate the rate of heating, as well as the maximum temperature, can be loaded with a number of crucibles containing filter paper and precipitates. Thus, the drying, charring, and final ignition of the precipitates can be done automatically so that the analyst can be released for other duties.

*Miscellaneous.*—Space in this text does not permit a detailed discussion of all the valuable electrical apparatus that is commercially available to aid the analyst in his work. A number of other important types are: the electrometric pH meter, filter photometers, spectrophotometers, potentiometric titration apparatus, fluorescent photometers, flame photometers, spectrographs, and various types of x-ray and radioactivity equipment.

### IMPORTANCE OF APPARATUS

Dr. G. E. F. Lundell, one of the most outstanding analytical chemists of this century, stated in 1933 in *Analysis of Things as They Are*,<sup>8</sup> "The mechanical details of quantitative analysis have been quite satisfactorily worked out; the chemical details have not. In other words, balances, weights, volumetric apparatus, reagents, glass, quartz, porcelain and platinum ware, filtering media, burners, ovens, and even procedures for the determination of elements when occurring by themselves need very little improvement for ordinary purposes. On the other hand, methods for the quantitative separation of the elements from one another are far from perfect. Far more poor determinations are caused by the use of faulty or unsatisfactory methods of analysis than by errors in weighing, measuring, or other manipulations. This is not intended to discourage proper attention to such considerations, but to urge that a little less attention be paid to the method of weighing and a little more to the thing that is weighed."

This statement was made more than a quarter of a century ago and it is still true. However, many of the fine points of the "so-called" mechanical details of quantitative analysis have been neglected and forgotten. Much of the disagreement in analytical results obtained by different laboratories can be eliminated if the proper attention is given to these fine details. This is especially true in the selection and proper use of standardized weighing and measuring apparatus.

<sup>8</sup> Lundell, G. E. F., *Ind. Eng. Chem., Anal. Ed.*, 15, 221, 1933.

## Chapter 2

# SAMPLING

### PURPOSES OF SAMPLING

*Judging Acceptability.*—Most often, a sample is taken because one wishes to know if the material it represents meets purchase or sales specifications. For this purpose, the sample must accurately represent the whole quantity under consideration. Frequently, more than one sample is needed and analyses must be performed on each of the samples that are taken. Sometimes it is possible to combine two or more samples for analysis, but it is always necessary in such cases that the samples be combined in the proper proportions and in a way that is consistent with the known or expected properties of the material.

*Detecting Contamination.*—Another facet of acceptance sampling is to assure the absence of contamination or dirt from the material being sampled. For this important (but restricted) purpose, it is usually preferable to sample in a way that gives maximum assurance of finding the contamination if any be present. Samples of this kind, therefore, do not accurately represent the entire quantity. For example, when foreign matter is suspected, one samples as near to the bottom of the container as possible. Similarly, when an easily oxidized product is thought to have been exposed to air, one samples at the surface. In both cases, the probability of detecting contamination is deliberately increased at the expense of obtaining truly representative samples. It is good practice to take representative samples first and then to take samples as needed to assure absence of contamination.

*Identifying Materials.*—A third purpose of sampling is to identify an unknown material. The expense of obtaining an accurate sample may not be warranted, and usually the question of possible contamination does not immediately arise. Very rarely, the choice among two or several possibilities is so close that only a carefully taken sample can adequately serve to establish identity.

# PROBABILITY SAMPLING OF MATERIALS

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## INTRODUCTION

A sample submitted to the laboratory for quantitative assay is assumed to be representative of the lot of material or product from which it was drawn. By "representative" we mean that the magnitude of the particular property being evaluated is the same in the sample as in the lot. For uniform materials such as a clear solution, any one portion is obviously a representative sample. Since for nonuniform materials no one portion or unit is likely to be representative, it is the usual practice to select a number of portions to constitute the sample, in the expectation that the average value of the property in the sample will be essentially the same as the average that would be found for the entire lot under the same conditions. How well this expectation is realized depends on the number of portions in the sample and how these portions are selected. Rule of thumb, judgment, and intuition are often relied upon for these purposes, but samples so drawn do not furnish an objective criterion for judging the result. A probability sample, on the other hand, does furnish criteria for estimating the sample size required and for judging the precision achieved.

A probability sampling plan is one that makes use of the theory of probability to combine a suitable procedure for selecting sample portions or items with an appropriate procedure for summarizing the test results, so that a valid objective evaluation may be made of the probable limits of sample error. Essential features of probability sampling of materials for determination of an average property are described in this section.

## THE CONCEPTS OF UNIVERSE AND SAMPLE UNITS

A lot of material or product is, or may be conceived as being, composed of  $N$  distinct portions or units, each possessing the given property but not necessarily to the same extent or magnitude. The units may be individual items such as electronic tubes or cakes of soap; packages of material such as bales of cotton or drums of oil; small quantities taken from a bulk commodity by means of a trier, thief, drill, scoop, shovel, or other sampling device. The numerical values of the property for all the units constitute a statistical universe having some form of distribution with a mean value and a variance. Any group of  $n$  units could be considered a sample of this universe. However, only if the  $n$  units have been independently selected at random is the resulting sample a probability sample. For such a sample certain statistics may be calculated from the test results, from which valid inferences may be drawn and objective answers given to a variety of

important questions. For example: What is the likelihood that a second probability sample of  $n$  units drawn from this lot will have an average value (or range of values, or percentage of defectives) which differs from that of the first sample by more than a specified amount?

Of major importance in a sampling plan is the determination of the number of units to be drawn such that sample averages will have a prescribed level of precision. Equations for calculating the required sample size are available when certain prior information exists.

### INFORMATION REQUIRED

For the calculation of minimum sample size, certain information is needed.

1. There must be an advance estimate of the standard deviation of the units in the universe sampled. This estimate may be derived in several ways:

(a) The process that produced the lot may be in statistical control, with known standard deviation.

(b) Estimates of standard deviation from samples of previous lots of like material sampled under essentially the same conditions may be available.

(c) From general knowledge as to the approximate range of the property, from its lowest to its highest value in the sample units, and as to the shape of the distribution, a sufficiently good advance estimate may usually be made. Thus, if the values run rather uniformly throughout the range,  $R$ , the standard deviation is about  $0.3 R$ ; if most of the values lies at one end of the range, it is about  $0.25 R$ ; and if the values are mostly in the middle of the range, the standard deviation is approximated by  $0.2 R$ .

(d) If the sample is for the estimation of fraction defective, the standard deviation is  $\sqrt{p'(1-p')}$ , where  $p'$  is the fraction defective in the lot.

2. The level of precision desired must be specified. That is, it must be decided (a) what difference can be tolerated between the estimate to be made from the sample and the result that would be obtained by testing every unit in the universe, and (b) what risk is acceptable that by chance the tolerance will be exceeded. In arriving at decisions on tolerance and risk, it must be borne in mind that the smaller the tolerance or the risk, the larger will be the sample size required.

### EQUATIONS FOR CALCULATING SAMPLE SIZE

*Single-Stage Sampling.*—The universe consists of  $N$  units,  $n$  of which will be drawn as the sample.

$$n = \left( \frac{t\sigma'}{E} \right)^2 \quad (2-1)$$

where  $n$  = the number of units to be selected at random,

$\sigma'$  = the advance estimate of the standard deviation,

$E$  = the difference that can be tolerated between the sample estimate and the universe value, and

$t$  = a factor corresponding to the acceptable risk of exceeding  $E$ .

Table 2-1 lists the value of  $t$  for several commonly accepted risks.

In Eq. 2-1, it is assumed that  $N$  is large compared to  $n$ . When this is not the

TABLE 2-1

$t$	Probability That $E$ Will Be Exceeded
3	3 in 1000
2.58	1 in 100
2	45 in 1000
1.64	1 in 10

case, the required sample size will be smaller than that indicated by Eq. 2-1. This smaller size,  $n_L$ , is given by Eq. 2-2.

$$n_L = \frac{Nn}{N + n} \quad (2-2)$$

**Two-Stage Sampling.**—Some lots of material are, or may be conceived as being, composed of two kinds of sample units, primary and secondary. Typical examples are: a shipment of yarn consisting of  $N_1$  cases (primary units), each containing  $N_2$  packages (secondary units); a lot of  $N_1$  bags (primary units) of fertilizer from each of which  $N_2$  trierfuls (secondary units) may be drawn. Other examples of primary units are the sublots of product or material produced at different times, or under different conditions; the individual carloads in a train; the quantities discharged from a bulk-weighing hopper, or from a conveyer belt in successive equal time periods. Both primary and secondary units constitute statistical universes. The number of secondary units required for a specified precision may be significantly less<sup>1</sup> in two-stage sampling than in single-stage sampling. A common type of two-stage sampling plan is the designation of the number,  $n$ , of primary units to be randomly selected from the lot and the number,  $k$ , of secondary units to be randomly drawn from each of the  $n$  selected primary units. The number,  $n$ , may be calculated from Eq. 2-3 when, as is usually the case,  $N_1$  is not very large compared to  $n$  and  $k$  is small compared to  $N_2$ .

$$n = \frac{N(\sigma_w'^2 + k\sigma_b'^2)}{kN\left(\frac{E}{t}\right)^2 + k\sigma_b'^2} \quad (2-3)$$

where  $n$  = the number of primary units to be selected at random,

$N$  = the number of primary units in the universe,

$k$  = the optional number of secondary units to be drawn at random from each of the  $n$  selected primary units,

$\sigma_w'$  = the advance estimate of the average standard deviation of the secondary units within the primary units,

$\sigma_b'$  = the advance estimate of the standard deviation of the primary units, and

$E$  and  $t$  are as previously defined.

From Eq. 2-3 it is evident that more than one value of  $n$  is possible for a specified precision, depending on the particular value of  $k$  preferred. Under a given

<sup>1</sup> By up to 41%, which occurs when the standard deviations of the primary and secondary universes are equal.



set of conditions, one value of  $k$  is most economical. This value,  $k_e$ , may be calculated from Eq. 2-4.

$$k_e = \frac{\sigma_w'}{\sigma_b'} \sqrt{\frac{C_1}{C_2}} \quad (2-4)$$

where  $C_1$  = average cost of selecting and handling a primary unit,  
 $C_2$  = average cost of taking and handling a secondary unit (including cost per test when the sample is not composited).

## ESTIMATION OF SAMPLE PRECISION FROM THE TEST RESULTS

Equations 2-1 and 2-3 are predictions of sample size required for a specified level of precision. They are based on advance estimates of the standard deviations. After a probability sample has been drawn, the actual sampling precision achieved may be judged, provided that each unit is tested individually. Equations 2-1 and 2-2 may be combined and rearranged as follows:

$$E = t\sigma \sqrt{\frac{N-n}{nN}} \quad (2-5)$$

Equation 2-3, when rearranged, is

$$E = t \sqrt{\frac{\sigma_b^2(N-n)}{Nn} + \frac{\sigma_w^2}{nk}} \quad (2-6)$$

In Eq. 2-5 and 2-6, the standard deviations are those calculated from the test data (corrected, if necessary, for the precision of the tests), so that the new value of  $E$  is independent of any error in the advance estimate.

## RANDOM SELECTION

Calculation of the precision of a sample is possible only if the selection of the sample units from a universe is made "at random." This term does not mean haphazardly; on the contrary, random selection is a definite, rigorous procedure which insures that each item or unit in the particular universe being sampled has an equal chance of being selected. The universally accepted process for random selection is the assignment of a unique number to each unit and the use of a table of random numbers to designate the specific units to be selected. Mechanical devices for generating random numbers, such as roulette wheels, cards, or dice, are acceptable provided they have been tested to assure the absence of bias. Numbering of units may be actual, as in serially numbered bales or other packages, or by rule. For packages stored in a warehouse, the rule might be based on serial numbering of rows, columns, and tiers. Similarly, within a package the rule might be based on the assignment of numbers to, say, front, middle, and back; top, middle, and bottom; and left and right. For random sampling at or through a surface, a set of templates with randomly located openings is often suitable. The particular process used in a given situation must be practicable and economical, but randomness in selection cannot be waived if known and controlled precision is to be achieved.

## DIFFICULTIES ENCOUNTERED IN PROBABILITY SAMPLING OF MATERIALS

Probability sampling is at times rather difficult or expensive. Some of the difficulties encountered, and how they may often be reduced or overcome are:

1. *Lack of Prior Information.*—There may be little information on the nature of the distribution of the desired property in the lot of material, or on the magnitude of the standard deviations. This is particularly true of raw materials and bulk commodities. The examination of previous data may often supply approximate but adequate estimates. Special statistical studies may be required. More and more, the results of such studies on a wide variety of products are being published and may be found to be applicable to the case at hand.

2. *Physical Difficulties.*—Because of the physical nature, condition, or location of the material at the time of intended sampling, the essential requirement of randomness in the selection of units may be impossible or economically not feasible. Units in the interior of a large pile of coal, for example, are not accessible and so do not have an equal chance of being drawn into the sample. Under such circumstances, no probability sample is possible. One solution to such a difficulty is to sample the material before it is piled up, while it is in motion, perhaps on a conveyer belt where random selection is possible. Planning for sampling at the proper time and place is too often overlooked.

3. *Excessive Cost.*—To achieve the desired and necessary degree of sample precision may require the selection of so large a number of units that the direct and indirect costs are prohibitive. Since the number increases as the square of the standard deviation, great economy results from the reduction of the variability between units. Mixing and blending are extremely effective in reducing variability but are infrequently possible with large lots of material. Two-stage sampling, especially where the most economical value of  $k_e$  has been calculated by Eq. 2-4, reduces sampling cost. For bulk materials, the nature of the sampling device and the procedure followed often have a great bearing on the variability of the units produced; for example, tubefuls taken perpendicular to the layers in a stratified liquid or powder have a lower standard deviation than (a) similar portions taken throughout the lot but parallel to the layers, or (b) the portions taken at random spots by means of a probe. Incidentally, it should be noted that if, in the preceding example, the layers are relatively uniform compared to the variability between layers, a reduction in tube diameter does not materially increase the standard deviation of the sample units but does effect a great reduction in their volume and weight. Finally, certain forms of transportation of some classes of material sometimes effect a mixing, sometimes a segregation. In the latter case, advantage may be taken of this condition to effect sample reduction by physically treating the lot as two sublots.

## PROBABILITY SAMPLING FOR PROPERTIES OTHER THAN AN AVERAGE

The preceding discussion has been concerned primarily with sampling for the determination of an average property, such as percentage of a constituent or Btu per pound. Probability sampling for the determination of other characteristics, such as degree of variability, has not been specifically covered. The general principles and practices outlined above are, however, applicable, and the mathematical

theory of probability can provide, for such samples, valid estimates of the precision achieved and the size of sample (number of units) required.

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# ***SAMPLING OF SOLIDS***

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## **INTRODUCTION**

Within the larger confines of activities that necessitate sampling, such as in problems of exploration, research, quality control, or the purchase and sale of materials, a specific purpose of sampling exists for each particular situation. For example:

1. One may wish to learn the average quality and the extremes of quality.
2. One may desire only to determine the fraction of the items that meet or fail to meet a specified requirement without regard to their average quality.
3. One may want to accumulate a series of test results to be used for a guide to rational action concerning a production process.

No single plan of sampling can meet these various situations most efficiently and economically, because of the many sampling techniques available for consideration in planning a sampling program. Nevertheless, the governing elements of any sampling situation can be summarized as follows:

1. The purpose of sampling.
2. The physical form in which the material is available.
3. The accuracy required in the sampling of the material.
4. The variability of the material to be sampled.
5. The minimum acceptable amount or weight of increment.
6. The minimum acceptable number of increments.
7. The minimum number of samples.
8. Preparation of the sample for subsequent testing.

These phases of the problem are inter-related, but can be considered separately to assess their individual significance.

The first three items cover known facts or decisions which influence the determination of the correct answers to items 5, 6, and 7, and sometimes 8. Item 4 must either be known or ascertained by appropriate means as discussed in the section on "Probability Sampling."

## **MINIMUM AMOUNT OR WEIGHT OF INCREMENT**

Sampling of solids that are uniform in size, such as standard size or king-size cigarettes of a particular brand, present no minimum weight problems in their selection for testing, but only the number which must be tested for the determination of quality for a particular lot.

In contrast, solids, such as unscreened crushed stone, have so many different-sized pieces that sampling by selection of individual pieces would be unwise if not impossible, since the sampler often has no way of knowing the relative pro-

portions of the various size pieces in the lot. The practical way of sampling solids composed of mixed sizes is by the removal of increments or portions from the lot by means of a shovel or scoop or by passing a collecting tub, trough, scoop, or bucket through a moving stream of the material. A mechanical arrangement for accomplishing this type of sampling is shown in Fig. 2-1.

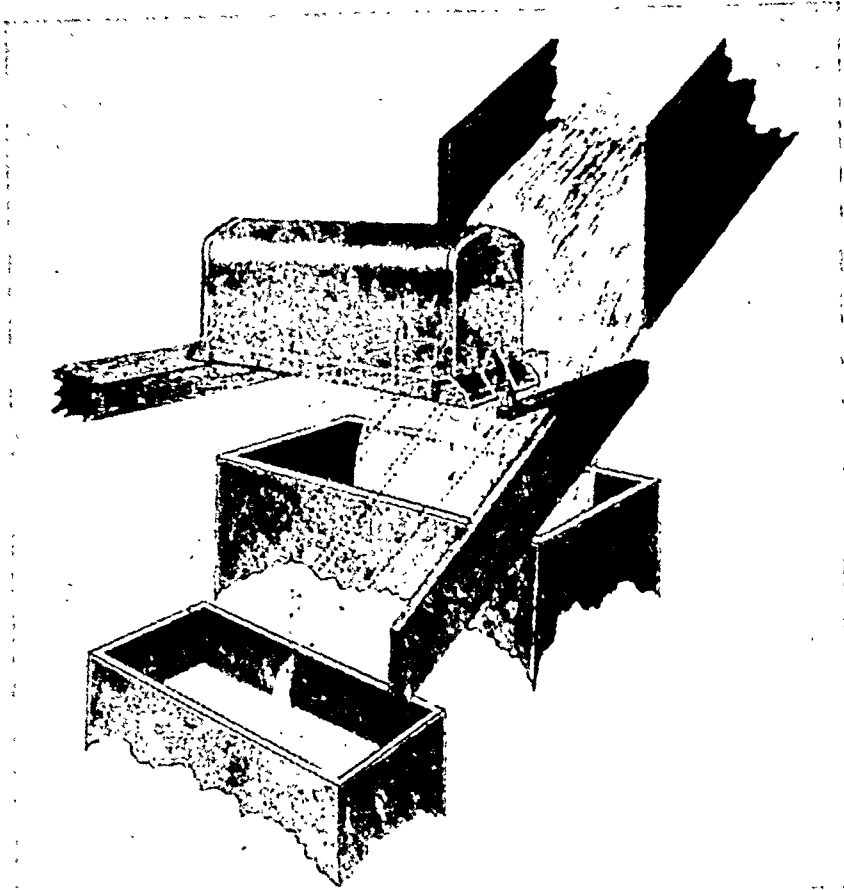


FIG. 2-1. Diagram of Arrangement for Sampling Dry Materials. Materials may be sampled falling from a chute as shown, or from a conveyor head pulley. (Courtesy of the Galigher Company.)

Accurate incremental sampling requires that the minimum weight of increment be sufficiently large so that all particles, regardless of size, have their fair chance of being included in the increment. In order to assure the attainment of this objective, the following two rules are used by experienced samplers for guides to minimum weight of increment:

1. When sampling from a moving stream by passing a collecting container through the stream, the inlet opening of the collecting container must be at least three times the size of the largest piece in the lot to be sampled.

2. When sampling aggregates at rest, as from a bin, the minimum weight of increment in kilograms must be 0.05 times the top particle size measured in millimeters.

## MINIMUM NUMBER OF INCREMENTS

Once an adequate weight of increment has been determined, the minimum number of increments to be analyzed separately can be learned by the use of Eq. 2-1, 2-2, 2-3, and 2-4 in the section on "Probability Sampling."

This procedure is rather simple to apply to discreet objects which are tested individually, as in the case of the determination of tensile strength of bolts or the compressive strength of concrete cylinders.

On the other hand, many materials are tested by analyzing a physical composite sample composed of a number of increments collected from various parts of a shipment and combined for their average chemical analysis. Examples are found in the analysis of steel drillings combined from a number of holes drilled in a specimen or in the analysis of an iron ore sample made up of the accumulation of a number of increments collected from the hold of a ship.

Combining increments physically into composite samples is an economical way of reducing the work load in a laboratory because it is obviously less work to make a single analysis for the average quality of a composite sample than to analyze each increment separately and average their results arithmetically. Yet, it is well to remember that the accuracy of the final average is not the same in the two cases because the variance of analysis prevents the average analysis of the composite sample from being as accurate as the arithmetic average of the analyses of the individual increments. In the latter case, the variance of analysis is reduced in accordance with the number of increments analyzed by the laboratory.

Many times the variance of analysis is relatively small in comparison with the total variance of the material; but large or small, the law of diminishing returns applies to the practice of combining increments into composite samples. The exact effect must be learned by trial with proper statistical interpretation.

Reflection on this truth leads to the additional conclusions that: <sup>†</sup> 4.

1. The greater the variance of analysis, the less benefit can be secured by combining an increasing number of increments.
2. The smaller the variance of the material sampled, the less benefit can be obtained by combining an increasing number of increments.

Thus, in cases where it is desirable to reduce analytical costs by analyzing composite samples, the variance of analysis should be determined in order to calculate the most economical number of increments in any particular sampling situation. Actually, of course, veteran samplers often know these numbers from experience. Unexperienced persons must make some tests to estimate the variances of analysis that accompany various types of materials.

## MINIMUM NUMBER OF SAMPLES

Many times the accuracy required in sampling is impossible to attain by the collection and analysis of a single sample because the variances of the material and/or the techniques of testing are so great that a single test on one discreet specimen, or a single test on a composite of many increments, will not provide a precision variance within the required variance. In such cases, additional samples must be tested.

This phase of sampling can be demonstrated in conjunction with the data in Table 2-2. Frequently, solid fuel contracts specify a change in price for every change in heat content of 25, 50, or 100 Btu. In terms of variance, these values are about 39, 156, and 625.

TABLE 2-2. HEAT CONTENT, BTU PER LB.

Increment	Test #1	Test #2	Difference	
1	14000	14020	+20	Vertical Variance = 7200 = Variance of Material Sampled.
2	14100	14080	-20	
3	14160	14140	-20	
4	14200	14220	+20	
Average	14115	14115		

Horizontal Variance = 200 =  
Analysis Variance

Total Variance = 7400 = observed Variance in each test run.

In order to determine the most economical number of increments and number of samples to test, a chart should be constructed from the known data. Figure 2-2 illustrates the problem, the results being plotted from Table 2-3 and the specified accuracy variances.

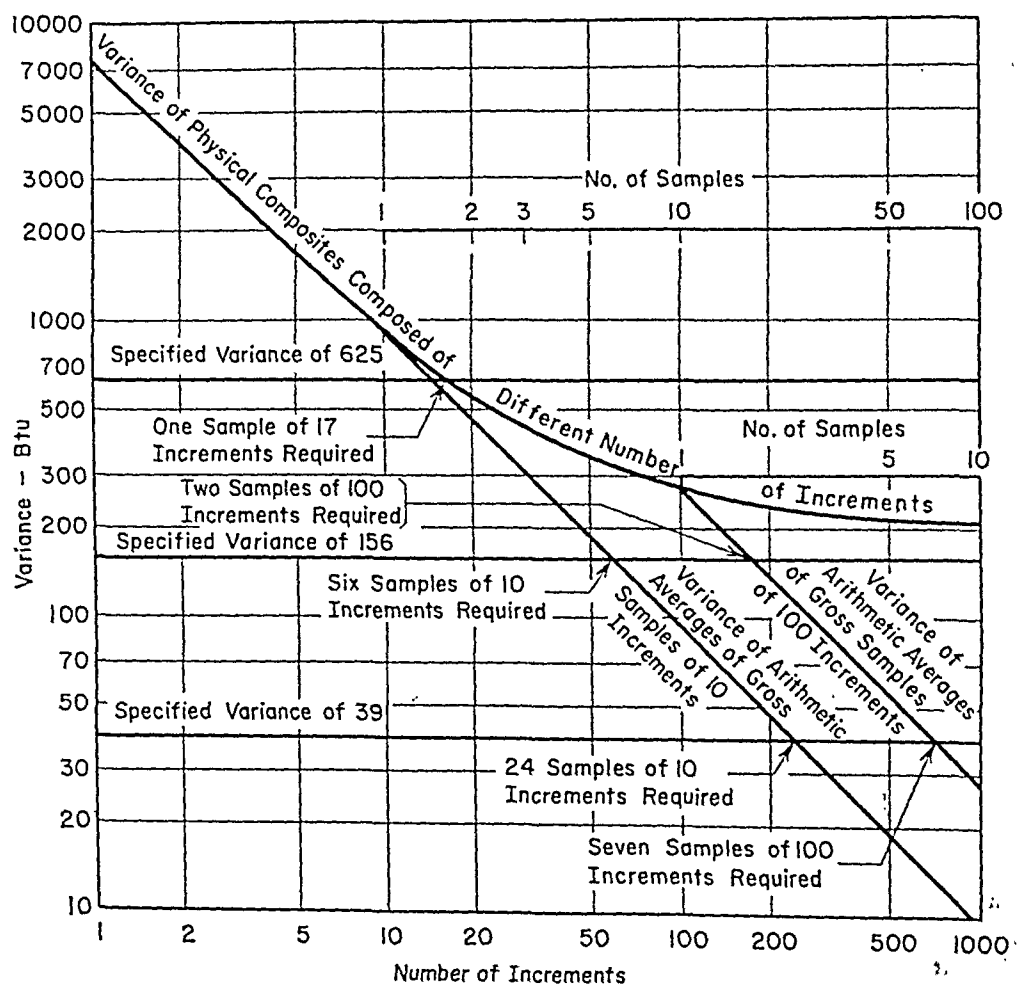


FIG. 2-2. Relation of Specified Variance to Number of Increments and Samples (Heat Content of Fuel—Btu). (Courtesy ASTM.)

TABLE 2-3. DISTRIBUTION OF VARIANCE ACCORDING TO NUMBER OF INCREMENTS COMPOSITED

$$S_s^2 = \frac{S_M^2}{N} + \frac{S_A^2}{1}$$

where  $S_M^2 = 7200$ , and  $S_A^2 = 200$

<i>No. of Increments</i>	
1	7200 + 200 = 7400
2	3600 + 200 = 3800
4	1800 + 200 = 2000
10	720 + 200 = 920
20	360 + 200 = 560
40	180 + 200 = 380
100	72 + 200 = 272
200	36 + 200 = 236
400	18 + 200 = 218
1000	7 + 200 = 207

Figure 2-2 is plotted on log-log graph paper, and all similar plots require the proper choice of the number of cycles as well as the ordinate and abscissa scales. Especially important is the need to adapt a superimposed scale and a new set of log cycles at the point coinciding with the choice of number of increments in the composited sample. This essential feature of the chart is shown by the different scales of number of samples applied to 10 and 100 increment composites, respectively. Points between the ends of cycles, such as 20 or 30 increments, require an overlay of fresh graph paper so that the beginning of a cycle will agree with the ordinate of the number of increments selected. Finally, it should be noted that the variance lines for arithmetic averages of the analyses of composite samples are drawn with a negative 45° line from the intercept of the ordinate of the selected number of increments with the asymptotic curve of variance of composites composed of different number of increments.

Figure 2-2 shows that a single gross sample composed of 17 increments will provide an answer within the specified variance of 625—that is, within a precision of 100 Btu. To get twice as precise an answer, or a result within 50 Btu or 156 variance, requires the analysis of at least two gross samples composed of a minimum of 100 increments or the analysis of more than two gross samples composed of fewer than 100 increments. For a precision of 25 Btu, equivalent to a variance of 39, four times as many gross samples are required as for 50 Btu.

Charts of this type are most useful to the solution of sampling problems wherein physical composites are the type of sample tested.

### PREPARATION OF SAMPLES

Many samples obtained from various types of material require a certain amount of preparation before subsequent testing. In this connection, it must be emphasized that preparation means the processing of samples in a manner that makes them more satisfactory for testing without changing their essential characteristics. For example, samples of steel drillings may be contaminated with cutting oil which



<i>Preparation</i> <i>Test No.</i>	$X_1$ <i>Analysis</i> <i>No. 1</i>	$X_2$ <i>Analysis</i> <i>No. 2</i>	$d$ <i>Diff.</i>	$X_1 + X_2$ <i>Sum</i>	$(X_1 + X_2)^2$ <i>(Sum)</i>	<i>Average</i>
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Knowledge of the values of the several variances in the foregoing equations is important to complete an understanding of any specific problem of sample preparation. On the other hand, such knowledge is not always available or obtainable at the moment, nor is it necessary to the design of many preparation procedures

TABLE 2-4. ANALYSIS OF VARIANCE OF TABLE 2-2 DATA

<i>Increment</i>	$X_1$ <i>Test</i> <i>No. 1</i>	$X_2$ <i>Test</i> <i>No. 2</i>	$d$ <i>Diff.</i>	$X_1 + X_2$ <i>Sum</i>	$(X_1 + X_2)^2$ <i>(Sum)<sup>2</sup></i>	<i>Average</i>
1	14000	14020	+20	28020	785,120,400	
2	14100	14080	-20	28180	794,112,400	
3	14160	14140	-20	28300	800,890,000	
4	14200	14220	+20	28420	807,696,400	
Total	56460	56460		112920	3,187,819,200/2 = 1,593,909,600	
Average	14115	14115			$\Sigma(X_1 + X_2)^2/8 = (112,920)^2/8 = 1,593,865,800$ *	
$\Sigma X^2$	796,955,600	796,954,800			Difference =	43,800 †
		796,955,600				
$\Sigma(\Sigma X_1^2$						
+ $\Sigma X_2^2)$						
= 1,593,910,400						(Total Sum of Squares—Uncorrected)
Correction Factor						
		1,593,865,800				
		44,600				(Total Sum of Squares—Corrected)

\* Correction factor

† Material

## COMPONENTS OF VARIANCE

<i>Source</i>	<i>Sum of</i> <i>Squares</i>	<i>Degrees of</i> <i>Freedom</i>	<i>Mean</i> <i>Square</i>
Total	44600	7	
Material + Analysis	43800	3	14600
Difference (Analysis)	800	4	200

$$\text{True Material Variance} = \frac{14600 - 200}{2} = 7200$$

$$\begin{aligned} \text{Unit Increment Variance} &= \text{Analysis Variance} + \text{True Material Variance} \\ &= 200 + 7200 \\ &= 7400 \end{aligned}$$

The equation is:

$$S_o^2 = S_A^2 + S_U^2 \quad \dots \dots \dots (4)$$

since experience has developed rule-of-thumb methods for guidance in preparing bulk materials for analysis.

**Rules for Bulk Sample Preparation.**—1. When the gross sample is several times larger than the product of the minimum weight of increment times the minimum numbers of increments due to physical conditions causing the weight of increments to be several times the required minimum weight, the gross sample may be resampled without previous crushing in order to reduce the weight of the gross sample, provided that:

- (a) The minimum number of increments in the resampled portion is at least as many as those required in the initial gross sample.
- (b) The minimum weight of the increment collected for the resampled portion is at least as much as the minimum weight required for the initial gross sample.
- (c) The size consist of the resampled portion is the same as that in the initial gross sample.

2. The particle size of the pulp to be furnished to the laboratory must be specified by the analyst. Chemical analyses usually require very fine size pulps such as 60-mesh  $\times 0$  for coal, 100 mesh  $\times 0$  for iron ore, or 200 mesh  $\times 0$  for silicate rocks. The rule to follow in cases of this kind is that the variance of reduction can be minimized by utilizing as few pieces of preparation equipment as possible, thereby limiting the number of operations.

For instance, a sample of 2 in.  $\times 0$  could be crushed to  $\frac{3}{8}$  in.  $\times 0$ , reduced in weight and recrushed to  $\frac{1}{8}$  in.  $\times 0$ , again reduced in weight and recrushed a second time to 20 mesh  $\times 0$ , reduced in weight a third time and finally pulverized to an acceptable particle size for the chemist.

If this four-stage method were supplanted by a two-stage method of crushing the 2 in.  $\times 0$  to  $\frac{1}{8}$  in.  $\times 0$  followed by weight reduction and final pulverization to the laboratory pulp, the variance of reduction would be improved. Ordinarily, an additional benefit results by minimizing the stages of preparation in that labor costs are reduced by curtailing the amount of material handling.

3. In contrast, some characteristics of materials may dictate stage preparation. For example, loss of moisture from coal or iron ore samples will occur during handling operations. Therefore, it is essential that wet samples be dried and the moisture loss recorded prior to crushing if moisture is important to the evaluation of the material.

4. At each stage of crushing, the retained weight of material after subdivision of the crushed product must be more than the weight required in a gross sample of the same top particle size. An example would be a required weight of gross sample of 25 lb. for a  $\frac{3}{8}$  in. top size of material which would mean that crushing of a 1 in. top size of a similar material to  $\frac{3}{8}$  in.  $\times 0$  would require at least 25 lb. in the retained portion of  $\frac{3}{8}$  in.  $\times 0$  after subdivision of the crushed product.

5. The crushers, pulverizers, and sample dividers used in bulk sample preparation should be designed to prevent loss of sample while in process and preclude bias due to particle segregation during subdivision. A corollary requirement is that all equipment should be constructed for easy access so that inspection and cleaning can be done with minimum dismantling of parts.

**Equipment.**—Many types of mechanical equipment are suitable and available for preparation of samples of bulk solids. Primary crushing of soft to medium hard materials is done most often with hammer mills, whereas harder materials usually

require jaw or gyratory crushers. Secondary crushing frequently can be accomplished with primary mills set to a smaller discharge opening. Roll mills are good for brittle materials, but not for tough tabular particles. Pliable solids, such as agricultural products, paper products, or woody products, need slicing or chopping mills. Fine grinding and pulverizing of soft or brittle materials can be effected by high speed hammer mills, but hard tough materials may require ball mills or even a mechanical mortar and pestle. All of these items are stocked by one or more of the large laboratory supply companies.

Equipment for subdividing or reducing the weight of sample also is available from one or more sources of manufacture or sale. Riffle splitters for manual division of bulk materials are probably used more than any other device for sample weight reduction because riffles are portable as well as cheap in comparison with the cost of mechanically powered dividers. Riffle splitters are stocked by most laboratory supply companies.

Mechanical sample dividers are machines which cause the sample to flow in a ribbon pattern (usually in a vertical direction) past some point in the machine where the ribbon of material can be intercepted periodically by a sample cutter. Essentially, there are three types of cutters which travel horizontally and at right angles to the streams of material being divided:

1. Reciprocating
2. Rotary
3. Combination reciprocating and rotary

Reciprocating cutters are mounted on, or suspended from, a horizontal shaft, and travel in a straight line back and forth through the stream. In contrast, rotary cutters are attached to a vertical shaft which revolves the cutter through the stream. Combination-type cutters are reciprocating flap gates which are hinged at one end and develop maximum travel at the other end. The diagrams in Fig. 2-3 demonstrate the flow of material through various types of mechanical dividers.

Any of these cutters will perform satisfactorily if correctly installed and properly maintained, provided that the variability in the ribbon of material intercepted by the cutter is sequential from start to finish rather than segregational from side to side of the flow. If the stream has segregation from side to side, reciprocating cutters should be used because their straight line movement cuts equal percentages from all parts of the intercepted band of material. Rotary cutters and flap gates generate pie-shaped cuts which can cause bias in the retained sample if segregation is present in the sample stream at the time of interruption by the cutter.

Unfortunately, the user seldom knows ahead of time that side to side segregation will not be present, nor can he be sure that periodic cyclical patterns of variability in the stream will not coincide with cutter movements. Hence, it is imperative that every installation for mechanical sample reduction to be checked for possible bias in operation.

**Equipment Check Tests.**—Several practical rules, learned from experience, have been accepted by veteran samplers as quick guides to acceptable design of machine splitters:

1. The minimum distance between cutting edges of the sample slot or cutter should be three times the maximum particle size of the material sampled.

2. The cutter should travel at a uniform rate through the whole stream and completely out of the stream at each sampling.

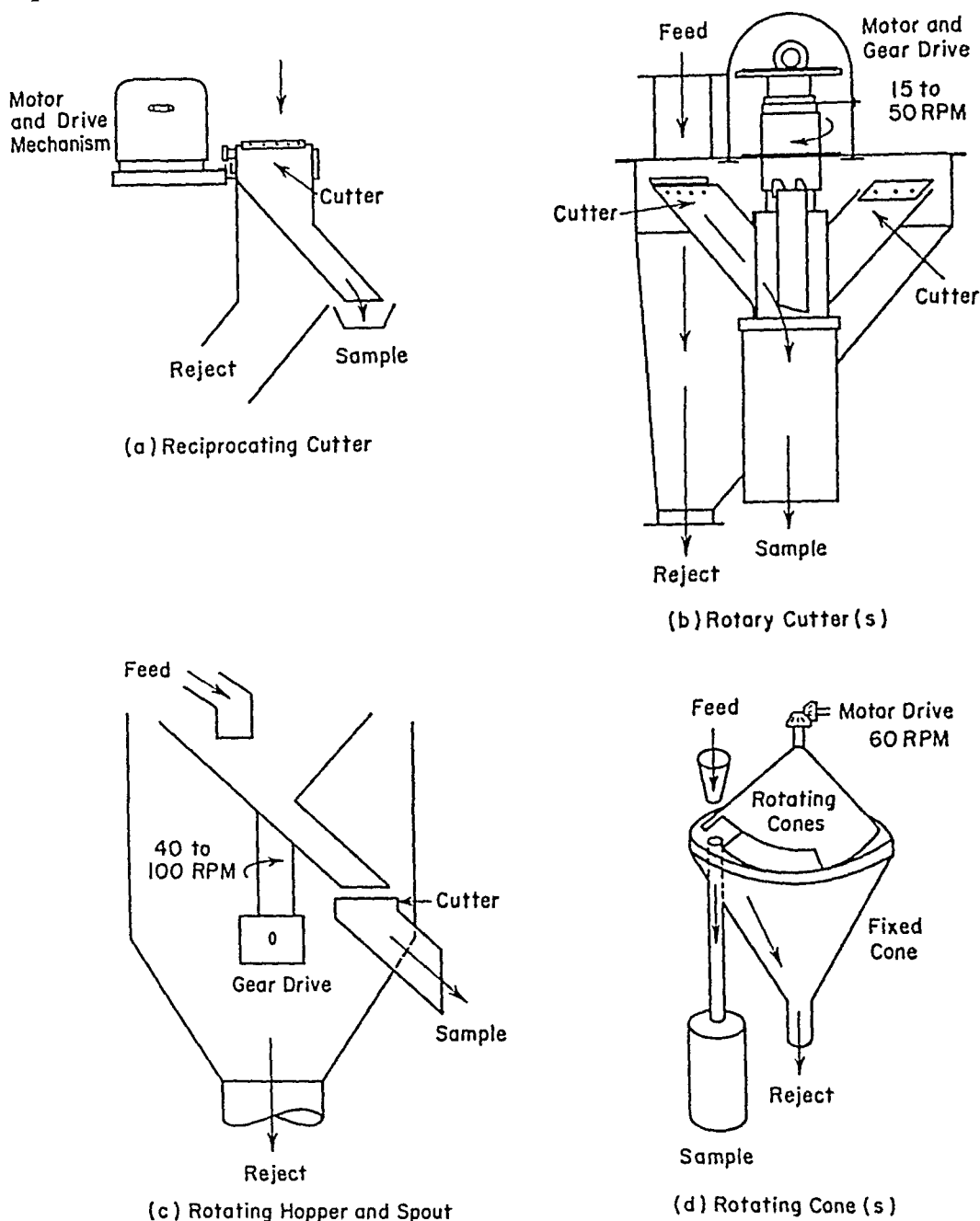


FIG. 2-3. Mechanical Sample Dividers. Proposed by ASTM Committee D-5. (Courtesy ASTM.)

3. The interval between cuts should be constant for any single sample reduction.

4. The depth of cutter should be large enough to prevent overflow.

5. The speed of the cutter must be adjusted to the flow of the stream to prevent overflow at too low speeds and to preclude splashing at too high speeds.

6. The feed to the cutter must be uniform and at a steady rate.

7. Spillage, drippage, or leakage of material into the cutter between sample periods must not occur.

In addition to these physical requirements for satisfactory machine sample dividers, the retained and reject portions from each machine should be tested regularly to determine that no significant difference in quality or size consist exists between them.

The definition of "significant difference" is a matter of personal opinion, for the simple reason that any difference can be proved to be significant statistically if sufficient data are gathered. Therefore, the evaluation of tests on retained and reject splits can be judged from experience with similar materials, or alternatively, a series of tests can be analyzed by statistical techniques known as "t" and "F" tests, the details of which can be learned from many textbooks on elementary statistics.

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# **SAMPLING OF LIQUIDS**

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## **GENERAL REQUIREMENTS AND PRECAUTIONS**

It will be the purpose of this chapter to describe adequate procedures for obtaining representative samples of homogeneous liquids under the most frequently encountered conditions. Samples taken in accordance with these procedures will be reliable enough to permit judging acceptability in terms of specifications; they will be more than adequately representative for identification purposes. Procedures that allow detection of the common contaminants (water and dirt) are also described.

The universal requirements for taking good samples are cleanliness, preservation of sample composition, positive identification of samples, and scrupulous care of sampling apparatus. Precautions that pertain to safety and the preservation of samples during handling, transportation, and storage must be observed at all times.

If sampling tasks are assigned to untrained personnel, there is a lively danger that the samples will not be representative. As a consequence, the effort of analysis and testing may be wasted and erroneous acceptance or rejection of material can result. The costs of wasted labor and material are usually sufficient to justify the necessary investment for properly training and equipping the sampling personnel. An analysis can be no more reliable than the sample; precision in sampling must precede precision in testing.

*Cleanliness* denotes the rigorous exclusion of foreign material from apparatus and containers before and during sampling. It is good practice to inspect all sampling devices and apparatus immediately before use to confirm that they have not gotten dirty or contaminated. Sampling connections should be rinsed and wiped externally just before use, and should be flushed internally with enough of the material to be sampled to displace the contents of the connections. The sampling apparatus should be filled and allowed to drain before drawing the actual sample. Likewise, the sample container should be rinsed and drained before it is filled with the actual sample.

Clean hands are important. Gloves should not be worn except when absolutely necessary, such as in cold weather, or when handling hot materials, or for reasons of safety. When gloves are necessary, clean gloves must be used.

*Preserving sample composition* requires knowledge, judgment, and skill. Volatile samples must be protected against evaporation. If the material being sampled contains solid particles or droplets of an immiscible liquid, care must be taken that all such particles or droplets are transferred to the sample container. The sample must not be allowed to solidify (or melt) during the sampling operation. Dissolved or entrained gases should not be allowed to escape, if they are present. Likewise, it is often important to avoid entraining air in the sample while transferring it from the apparatus to the final container.

**Identification** of samples must be complete, clear, and permanent. Label the container immediately after a sample is obtained. Use waterproof and oil-proof ink or a pencil hard enough to dent the tag, since soft pencil and ordinary ink markings are subject to obliteration from moisture, smearing, and handling. Include the following information:

- Date and time (and for continuous and dipper samples the hour and minute of collection);
- Name of the sampler;
- Name or number and owner of the container;
- Brand and grade of material; and
- Reference symbol or identification number.

**Handling and transporting samples** properly entails protection against breakage, evaporation, leakage, exposure to light, and entry of dust or moisture. To allow for expansion and contraction of the liquid, never fill a sample container more than 80% full. To protect against evaporation and leakage or the entry of moisture or dust, cover the stoppers of glass bottles with plastic caps that have been swelled in water and wiped dry; place the caps over the tops of the stoppered bottles and allow them to shrink tightly in place. Tins and cans may be similarly protected by an inner sealing disk tightly inserted in the opening; the screw cap is then tightened securely. If the material is known to be light-sensitive, or even not known not to be light-sensitive, opaque containers or brown bottles should be used. If clear bottles are used of necessity, they should be wrapped with opaque paper immediately. Samples should be packed in cartons or boxes as a precaution against breakage or other damage.

## TERMINOLOGY

There are several different kinds of samples that may be used separately or composited to represent the entire quantity of liquid being examined:

**An Average Sample** is one that consists of proportionate parts from all sections of the container.

**An All-Levels Sample** is one obtained by submerging a closed sampler to a point as near as possible to the draw-off level, then opening the sampler and raising it at a rate such that it is about  $\frac{3}{4}$  full as it emerges from the liquid. An all-levels sample is not necessarily an average sample, because the tank volume may not be proportional to the depth and because the operator may not be able to raise the sampler at the variable rate required for the proportionate filling. The rate of filling is proportional to the square root of the depth of immersion. The tube sampling procedure (see page 45) may be used to obtain an all-levels sample from a barrel or drum.

**An Upper Sample** is one obtained from the middle of the upper third of the tank contents, Fig. 2-4.

**A Middle Sample** is one obtained from the middle of the tank contents, Fig. 2-4.

**A Lower Sample** is one obtained from the middle of the lower third of the tank contents, Fig. 2-4.

**A Single Tank Composite Sample** is a blend of the upper, middle, and lower samples. For a tank of uniform cross-section, such as an upright cylindrical tank, the blend consists of equal parts of the three samples. For a horizontal cylindrical tank, the blend consists of the three samples in the proportions shown in Table 2-5.

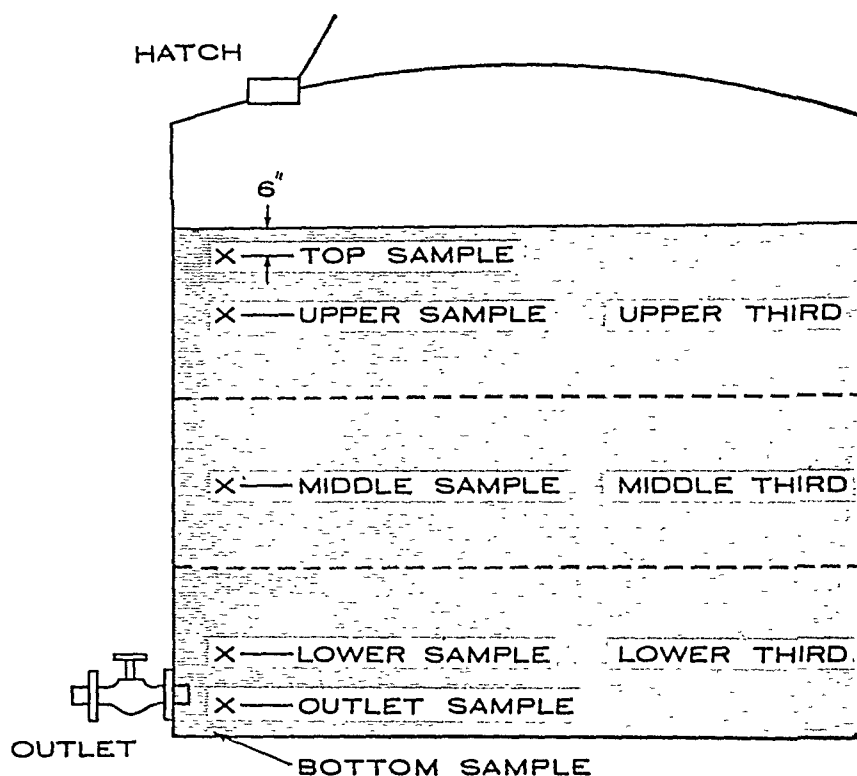


FIG. 2-4. Sampling Depths. (Courtesy ASTM.)

TABLE 2-5. SAMPLING INSTRUCTIONS FOR HORIZONTAL CYLINDRICAL TANKS

Liquid Depth, Per Cent of Diameter	Sampling Level, Per Cent of Diameter Above Bottom			Composite Sample, Proportionate Parts of		
	Upper	Middle	Lower	Upper	Middle	Lower
100	80	50	20	3	4	3
90	75	50	20	3	4	3
80	70	50	20	2	5	3
70	—	50	20	—	6	4
60	—	50	20	—	5	5
50	—	40	20	—	4	6
40	—	—	20	—	—	10
30	—	—	15	—	—	10
20	—	—	10	—	—	10
10	—	—	5	—	—	10



*A Multiple Tank Composite Sample (Ship, Barge, etc.)* is a blend of individual all-level samples, from each compartment that contains the liquid being sampled, in proportion to the volume of material in each compartment.

*A Top Sample* is one obtained 6 in. below the top surface of the tank contents, Fig. 2-4.

*An Outlet Sample* is one obtained at the level of the tank outlet (either fixed or a swing line outlet), Fig. 2-4.

*A Continuous Sample* is one obtained from a pipeline conveying the material in such manner as to give a representative average of the stream throughout the period of transit.

*A Dipper Sample* is one obtained by placing a dipper or other collecting vessel into the path of a free-flowing stream so as to collect a definite volume from the full cross-section of the stream at regular time intervals for a constant rate of flow, or at some time interval varied in proportion to the rate of flow.

*A Mixed Sample* is one obtained after mixing or vigorously stirring the contents of the original container, and then pouring out or drawing off the quantity desired.

*A Tube or Thief Sample* is one obtained with a sampling tube or special thief, either as a core sample, or a spot sample from a specified point in the container.

*A Drain Sample* is one obtained from the draw-off or discharge valve. Occasionally, a drain sample may be the same as a bottom sample, as in the case of a tankcar.

*A Bottom Sample* is one obtained from the material on the bottom surface of the tank, container, or line at its lowest point, Fig. 2-4. (Drain and bottom samples are usually taken to check for water, sludge, scale, etc.)

## MANUAL SAMPLING PROCEDURES

In this section are outlined five commonly used procedures for sampling homogeneous liquids. The first two (bottle sampling and tap sampling) are almost solely for taking representative samples. The third and fourth (thief sampling and tube sampling) are useful for detecting contamination and are also suitable under proper circumstances for taking representative samples. The fifth (dipper sampling) is useful for sampling open streams, and is most often employed when one wishes to obtain an instantaneous or "grab" sample.

These procedures are adequate for normal sampling needs, but no attempt is made to cover unusual situations. Alertness, care, and good judgment must be constantly exercised to recognize and deal with unexpected conditions.

*The Bottle-Sampling Procedure* is applicable for sampling liquids in tanks, tanktrucks, tankcars, ships, and barges. Solids or semiliquids that can be liquefied by heat may be sampled by this procedure provided they are liquids at the time of sampling. A suitable sampling bottle assembly is shown in Fig. 2-5. The open neck of the bottle should be at least  $\frac{3}{4}$  in. in diameter for liquids of low viscosity, such as aromatic solvents, most aqueous solutions, gasoline, kerosene, and diesel fuels. The opening should not be less than  $1\frac{1}{2}$  in. in diameter for sampling more-viscous materials such as lubricating oils, fuel oils, plasticizers, and thixotropic suspensions.

*All-Levels Sample.* Lower the weighted, stoppered bottle as near as possible to the draw-off level, pull out the stopper with a sharp jerk of the cord or chain (nonsparking), and raise the bottle at such a rate that it is about  $\frac{3}{4}$  full as it emerges from the liquid. Stopper and label the bottle immediately.

Upper, Middle, and Lower Samples. Lower the weighted, stoppered bottle to the proper depths, Fig. 2-4, which are as follows:

- Upper sample . . . . . middle of upper third of the tank contents.
- Middle sample . . . . . middle of the tank contents.
- Lower sample . . . . . middle of lower third of the tank contents.

Pull out the stopper with a sharp jerk of the cord or chain (nonsparking) and allow the bottle to fill completely at the selected level, as evidenced by the cessa-

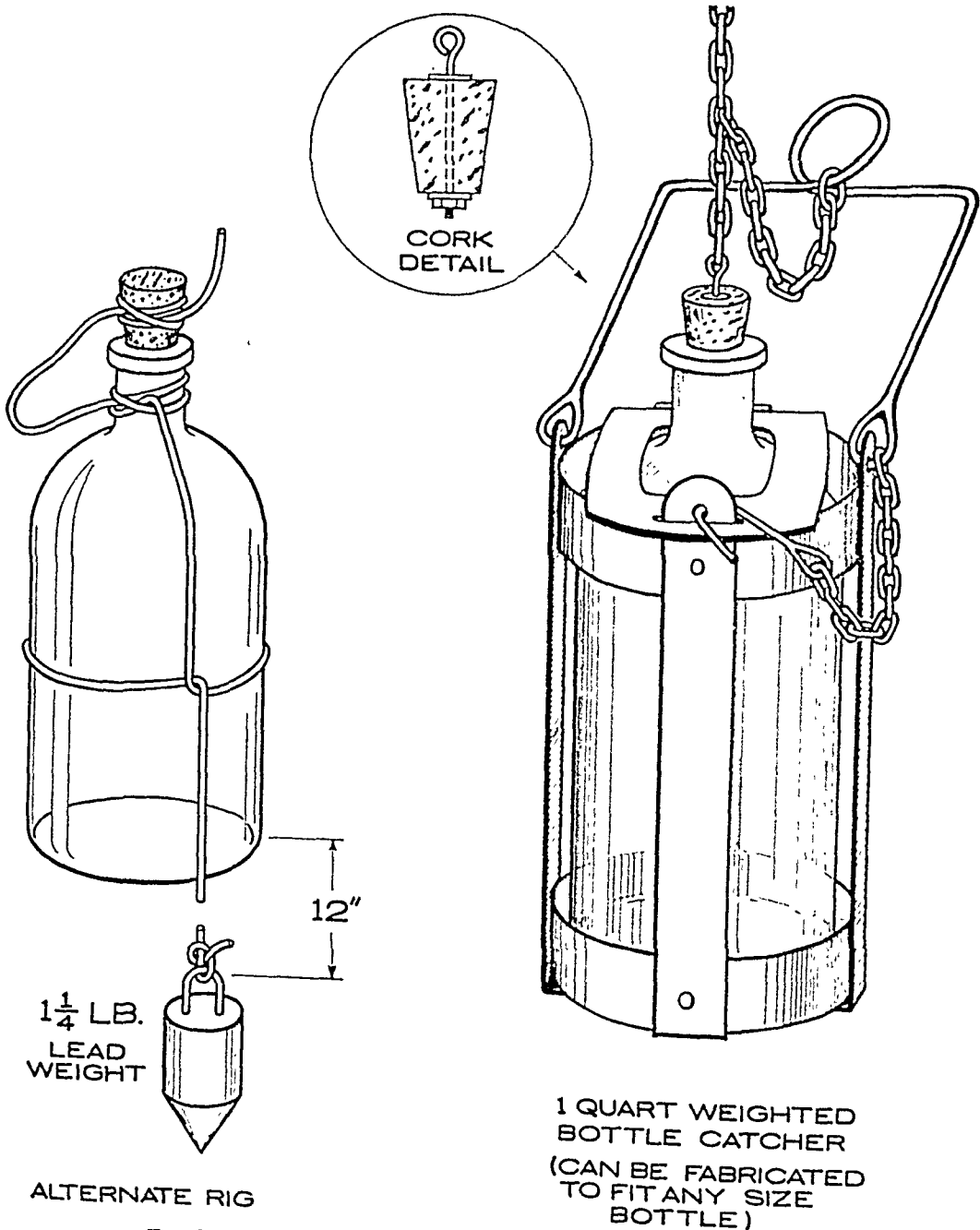


FIG. 2-5. Assembly for Bottle Sampling. (Courtesy ASTM.)

to opposite sides of the tube at the upper end are convenient for holding it by slipping two fingers through the rings, thus leaving the thumb free to close the opening.

To sample a barrel or a drum, stand it upright and sample from the top. If the detection of water, rust, or other insoluble contaminants is desired, let the barrel or drum remain in this position long enough to permit the contaminants to settle. Remove the bung and place it beside the bung hole with the oily side up. Close the upper end of the clean, dry sampling tube with the thumb, and lower the tube into the oil for a depth of about 1 ft. Remove the thumb, allowing oil to flow into the tube. Again close the upper end with the thumb and withdraw the tube. Rinse the tube with the oil by holding it nearly horizontal and turning it so that the oil comes in contact with that part of the inside surface which will be immersed when the sample is taken. Avoid handling any part of the tube that will be immersed in the oil during the sampling operation. Discard the rinse oil and allow the tube to drain. Insert the tube into the oil again, holding the thumb against the upper end. (If an all-levels sample is desired, insert the tube with the upper end open.) When the tube reaches the bottom, remove the thumb and allow the tube to fill. Replace the thumb, withdraw the tube quickly and transfer the contents to the sample container. Do not allow the hands to come in contact with any part of the sample. Close the sample container; replace and tighten the bung in the drum or barrel. Label the sample container and deliver it to the laboratory.

Obtain samples from cans of 5-gal. capacity or larger in the same manner as from drums and barrels, using a tube of proportionately smaller dimensions.

For cans of less than 5-gal. capacity, use the entire contents as the sample, selecting cans at random as indicated in Table 2-6 or in accordance with agreement between the purchaser and the seller.

TABLE 2-6. MINIMUM NUMBER OF PACKAGES TO BE SELECTED FOR SAMPLING

No. of Packages in the Lot	No. of Pack- ages to Be Sam- pled	No. of Pack- ages in the Lot	No. of Packages to Be Sampled	No. of Pack- ages in the Lot	No. of Packages to Be Sampled
1 to 3	all	513 to 729	9	2745 to 3375	15
4 to 64	4	730 to 1000	10	3376 to 4096	16
65 to 125	5	1001 to 1331	11	4097 to 4913	17
126 to 216	6	1332 to 1728	12	4914 to 5832	18
217 to 343	7	1729 to 2197	13	5833 to 6859	19
344 to 512	8	2198 to 2744	14	6860 or over	20

*The Dipper Sampling Procedure* is applicable for sampling liquids and semi-liquids where a free or open discharge stream exists, as in small filling and transfer pipelines (2 in. diameter or less) and filling apparatus for barrels, packages, and cans.

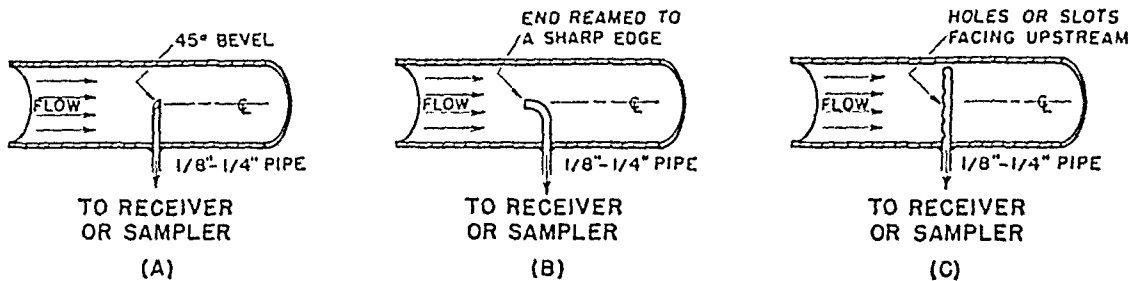
Use a *dipper* with a flared bowl and a handle of convenient length, made of material such as tinned steel that will not affect the product being tested. It should have a capacity suitable for the amount to be collected (see next paragraph) and must be protected from dust and dirt when not being used.

Insert the dipper in the free-flowing stream so that a portion is collected from the full cross-section of the stream. Take portions at time intervals chosen to collect a complete sample proportional to the quantity transferred. The gross amount of sample collected should be approximately 0.1%, but not more than 40 gal., of the total quantity being sampled. Transfer the portions into a clean, dry sample container of the desired size as soon as collected. Keep the container closed, except when pouring a dipper portion into it.

As soon as all portions of the sample have been collected, close and label the sample container, and deliver it to the laboratory.

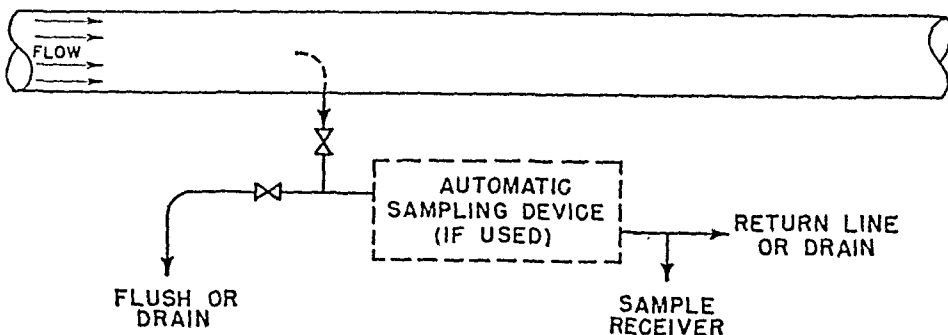
## CONTINUOUS SAMPLING

A number of mechanical sampling devices are in accepted use to withdraw samples from streams flowing in pipes. Where samples are needed from continuous processes, or to represent very large volumes (such as pipeline batches or transfers to or from tankships), automatic samplers are nearly indispensable. An installation for continuous sampling comprises



NOTE: PROBE MAY BE FITTED WITH VALVES OR PLUG COCKS.  
PROBE MAY BE DISPOSED HORIZONTALLY OR VERTICALLY.

### PROBES FOR CONTINUOUS SAMPLING



(D) TYPICAL ASSEMBLY FOR CONTINUOUS SAMPLING

FIG. 2-8. Continuous Sampling.

A *sampling probe* to withdraw from the flow stream a portion that will be representative of the entire stream. Commonly used probe designs are as follows:

(1) A tube extending to the center of the line and beveled at a 45° angle facing upstream.

(2) A long-radius forged elbow or pipe-bend extending to the center line of the pipe and facing upstream. The end of the probe should be reamed to give a sharp entrance edge.

(3) A tube extending across the pipeline with holes or slots facing upstream. The position and size of the probe should be such that it will minimize stratification and the dropping-out of heavier particles within the tube as well as displacement of oil within the tube as a result of variations in gravity of the flowing stream.

(4) To control the rate at which the sample is withdrawn, the probe or probes should be fitted with valves or plug cocks.

**Automatic Sampling Devices** may be classified under the following headings:

**Time Cycle (Nonproportional) Continuous Sampler.** A sampler designed and operated in such a manner that it transfers equal increments of liquid from the pipeline to the sample container at a uniform rate of one or more increments per minute is defined as a continuous sampler.

**Time Cycle (Nonproportional) Intermittent Sampler.** A sampler that is designed and operated in such a manner that it transfers equal increments of liquid from a pipeline to the sample container at a uniform rate of less than one increment per minute is defined as an intermittent sampler.

**Flow-Responsive (Proportional) Sampler.** A sampler that is designed and operated in such a manner that it will automatically adjust the quantity of sample in proportion to the rate of flow is defined as a flow-responsive (proportional) sampler. Adjustment of the quantity of sample may be made either by varying the frequency of transferring equal increments of sample to the sample container, or by varying the volume of the increments while maintaining a constant frequency of transferring the increments to the sample container.

**The Receiver** is a clean, dry container of convenient size to receive the sample. All connections from the sample probe to the sample container must be free of leaks. Two types of container may be used, depending upon service requirements:

**Atmospheric Receiver.** The atmospheric receiver is constructed in such a way that it retards evaporation loss and protects the sample from extraneous material such as rain, snow, dust, and trash. The construction should permit cleaning, interior inspection, and complete mixing of the sample prior to removal. The receiver should be provided with a suitable vent.

**Closed Receiver.** The closed receiver is constructed in such a manner that it prevents evaporation loss. The construction must permit cleaning, interior inspection, and complete mixing of the sample prior to removal. The receiver should be equipped with a pressure relief valve.

**A Nonautomatic Sample.**—To obtain a *nonautomatic sample*, adjust the valve or plug cock from the sampling probe so that a steady stream is drawn from the probe. Wherever possible the rate of sample withdrawal should be such that the velocity of liquid flowing through the probe is approximately equal to the average linear velocity of the stream flowing through the pipeline. Measure and record the rate of sample withdrawn as gallons per hour. Divert the sample stream to the sampling container continuously or intermittently, to provide a quantity of sample that will be of sufficient size for analysis. Label the sample and deliver it to the laboratory in the container in which it was collected.

**An Automatic Sample.**—To take an *automatic sample*, purge the sampler and the sampling lines immediately before the start of the sampling operation. If the sampler design is such that complete purging is not possible, circulate a continuous stream from the probe past or through the sampler. Withdraw the sample from the side stream through the automatic sampler, using the shortest possible connections. Adjust the sampler to deliver not less than one and not more than 40 gal. of sample during the desired sampling period. For time-cycle samplers, record

the rate at which sample increments were taken per minute. For flow-responsive samplers, record the proportion of sample to total stream. Label the samples and deliver them to the laboratory in the containers in which they were collected.

When sampling semiliquids, heat the sampler lines, sampler, and receiver to a temperature just sufficient to keep the material liquid and to assure accurate operation of the sampling devices.

*Deviations in Quantity of Sample.*—For time-cycle samplers, deviations in quantity of the sample taken should not exceed  $\pm 5\%$  of the average rate for a given setting. For flow-responsive samplers, the deviation in quantity of sample taken per thousand gallons of flowing stream should not exceed  $\pm 5\%$  of the chosen average.

## SAMPLING HETEROGENEOUS LIQUIDS

By far the most difficult sampling problems are those involving heterogeneous liquids. These problems are encountered more often than at first might be supposed. The most common case is that of estimating the amount of contamination in a nominally homogeneous fluid, after contamination has been found. Similarly, one may wish to know if undissolved solids or unreacted liquids are present at a given stage in the processing of a material. Samples are sometimes needed to study progress in the settling of a mixture.

Unfortunately, there are no established procedures for obtaining representative samples from multiphase liquids or liquid:solid mixtures. Increasing attention is being given to this type of problem, but very little is known about any except the simplest cases.

For relatively small quantities, very vigorous mixing can be employed just prior to sampling by one of the procedures described under "Manual Sample Procedures." This expedient is limited to cans, drums, and very small tanks. It is good practice to obtain at least three samples and perform separate analyses on each, in order to give added confidence to the result obtained.

When sampling from a flowing stream that is known to contain suspended solids or immiscible liquids, it is best to separate the suspended material and to collect only the desired liquid. If one cannot avoid the problem of taking a representative sample from such a stream, consideration has to be given to the linear flow rate of the stream, the linear flow rate in the sampling probe, the concentration of the particles, their density, average size and size distribution, and the location and design of the sampling probe. Each instance must be studied separately, and only experimentation can be relied on to provide satisfactorily designed installations.

The most recent research on this type of problem has been supported by the American Petroleum Institute and is referenced in the bibliography for this chapter.

## STATISTICAL SAMPLING PLANS

A great deal of attention has been directed since about 1939 to schemes for increasing the usefulness of samples in assaying average quality and detecting faulty units in production lots. Probability and statistics form the mathematical basis for these schemes. Very substantial amounts of time and effort, not only for sampling but more importantly for analysis, are conserved by applying these principles.

Statistical plans, typically, are designed for mechanical operations with great repetitiveness but are equally applicable to sampling a continuous process that involves liquids, or to sampling discrete small volumes such as cans or aerosol containers.

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## ***SAMPLING OF GASES***

See Chapter 35, Analysis of Fuel Gases and Related Products.

## Chapter 3

# DETECTION OF THE CATIONS AND ANIONS

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## SPOT TESTS\*

*Introduction.*—The selection of the tests used in preparing this section has been based largely on considerations of sensitivity and selectivity. In addition, tests generally have been preferred where the necessary reagents are likely to be available or easily prepared. In general, the most selective tests are the ones recommended, even though more sensitive tests are sometimes available.

Very few qualitative tests are applicable to solutions which might contain any or all cations: consequently most tests, even with selective reagents, require either a prior separation from possible interferences or the use of suitable masking reagents. Important exceptions, of course, occur in testing special materials where ions known to interfere are almost certainly absent. Thus, in establishing the identity of a pure substance, interference is rarely encountered. Further, in a problem calling for the identification of an element, such as molybdenum in steel, no serious consideration need be given to possible interference by metals such as gold, platinum, and ruthenium, since it is highly unlikely that any of these elements would be encountered in the analysis of steel.

It should be further noted that in selecting a method for the detection of an element, categorical statements regarding possible interference are frequently meaningless unless the quantity of foreign element present is defined. Therefore, no single set of tests can provide the solution to all analytical problems.

In the tests described below, an effort has been made to include those methods in which there is a minimum of interference by elements likely to be present along with the element sought. This applies particularly to elements that are

\* The tests described in this section have been adapted from tables prepared for the Handbook of Analytical Chemistry, edited by L. Meites, to be published by McGraw-Hill Book Co., New York. Some tests are based on information provided by Philip West, Louisiana State University.

chemically similar, or which belong to the same analytical group. For example, in selecting a test for cadmium it is desirable that lead, bismuth, and copper do not interfere, since all these ions are precipitated by hydrogen sulfide from a hydrochloric acid solution and the sulfides are not dissolved by ammonium sulfide or sodium hydroxide. In other words, if a simple sulfide separation is used to separate cadmium prior to confirming its presence, lead, bismuth, and copper will also be present if contained in the original sample. Interference by the alkaline earth metals, on the other hand, would be far less serious, since cadmium could readily be separated from these elements with the aid of hydrogen sulfide.

To aid the analyst in devising simple methods for the separation of the ions to avoid possible interference, the classical division of the elements into analytical groups is given in this chapter (page 63). A more complete separation of the individual ions is also described in the scheme of qualitative analysis by Noyes and Bray (page 64).

A number of books and reports are available which give a more detailed discussion of the detection of the individual cations and anions.<sup>1</sup>

**Detection of the Cations.**—The procedure for each test, its sensitivity, interference, and other information relating to the test is presented in the following style:

Element (or ion) Detected. Reagent(s) (Technique). Procedure. Result observed. Limit of identification (or dilution limit). Interfering substances (method or reagent used to eliminate interference shown in parentheses.)

The following abbreviations are used to indicate the technique used: C, crucible; FP, filter paper; M, microscope; S, slide; SP, spot plate; TT, test tube; WG, watch glass.

**Aluminum.** *Alizarin*(SP). 1 drop 1 *N* NaOH test solution ( $\text{AlO}_2^-$ ) + drop 0.1% reagent solution. Add 1 *N* HAc to discharge violet color. Then 1 drop 1 *N* HAc. Red precipitate or color. Run blank with 1 *N* NaOH. Sensitivity: 0.65  $\mu\text{g}$ . Interference:  $\text{Fe}(\text{NaOH})$ ,  $\text{Co}(\text{NaOH})$ ,  $\text{Cu}(\text{NaOH})$ , alkaline earth metals in concentrated solutions, Ga,  $\text{Ce}(\text{III})$ , Be, Ni, Ti, Zr, Th,  $\text{MoO}_4^{=}$ , V,  $\text{F}^-$ .

**Ammonia** ( $\text{NH}_4^+ + \text{OH}^-$ , heat). *Litmus paper*. Heat solid  $\text{NH}_4^+$  salt or test solution with 1 drop 2 *N* NaOH at 40°C. for 5 minutes in closed vessel in which is suspended a strip of moist red litmus. Change to blue. Run blank. Sensitivity: 0.01  $\mu\text{g}$ . Interference:  $\text{CN}^-(\text{Hg}^{++})$ . Alkali metals do not disturb.

**Ammonium.** *p*-Nitrobenzenediazonium chloride(SP). 1 drop test solution + 1 drop reagent (dissolve 1 g. *p*-nitraniline in 20 ml.  $\text{H}_2\text{O}$  + 2 ml. dil. HCl. Add 160 ml.  $\text{H}_2\text{O}$  with stirring. Cool, add 20 ml. 2.5%  $\text{NaNO}_2$ . Stir. Filter.) Place solid CaO (size of pea) between drops. Red color immediate. Run blank. Sensitivity: 0.7  $\mu\text{g}$ . Alkali metals do not interfere.

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✓ **Antimony.** *Rhodamine B (SP)*. In test tube, 5 drops 1:3  $\text{H}_2\text{SO}_4$  + 1 drop test solution + 1 drop 10% KI + 1 ml. benzene. Shake. On spot plate, 2-3 drops benzene extract + 1 drop 0.2% reagent solution. Violet benzene layer. Sensitivity: 0.25  $\mu\text{g}$ . Interference:  $\text{NO}_2^-$  (urea), oxidizing agents ( $\text{Na}_2\text{SO}_3$ ).

✓ **Arsenic (III and V).** *Zn + HCl + AgNO<sub>3</sub> (TT and FP)*. In a test tube place 1 drop test solution + few grains metallic Zn and 3 drops 1:3  $\text{H}_2\text{SO}_4$ . Insert in top of the tube cotton soaked with 15%  $\text{Cu}_2\text{Cl}_2$  in 10 N HCl and cover tube with filter paper impregnated with 20%  $\text{AgNO}_3$  solution. Brown-black stain. Sensitivity: 2.5  $\mu\text{g}$ . Interference: Hg(II) may in large amount. If  $\text{S}^{=}$ ,  $\text{SCN}^-$ ,  $\text{S}_2\text{O}_3^{=}$  and Sb are absent,  $\text{Cu}_2\text{Cl}_2$  need not be used. If Al + KOH are used instead of Zn + HCl, As(V) and Sb are not reduced; hence, As(III) is detected in presence of As(V).

✓ **Barium.** *H<sub>2</sub>SO<sub>4</sub> + KMnO<sub>4</sub> (TT)*. In small centrifuge tube place 1 drop test solution and 3 drops cold, saturated  $\text{KMnO}_4$  + 2-3 drops 1 N  $\text{H}_2\text{SO}_4$ . At once add dropwise saturated aqueous  $\text{SO}_2$  to decolorize solution. Centrifuge. Purple precipitate (observe against white background with magnification). Sensitivity: 2.5  $\mu\text{g}$ . Interferes: Pb. Do not interfere: Ca, Sr, Mg.

✓ **Beryllium.** *Morin (SP and FP)*. 1 drop neutral or slightly acidic test solution on spot plate + 3 drops cold saturated solution of  $\text{Na}_2\text{EDTA}$  in 1:10  $\text{NH}_3$  + 1 drop 0.02% reagent in acetone. Filter, wash precipitate with 2 drops EDTA solution, then  $\text{H}_2\text{O}$ , finally acetone. Filter paper shows green-yellow fluorescence with ultraviolet light. Sensitivity: 0.07  $\mu\text{g}$ . Interference: Zr.

✓ **Bismuth.**  *$\text{SnCl}_2$  + NaOH + PbCl<sub>2</sub> (SP)*. 1 drop HCl test solution + 1 drop saturated  $\text{PbCl}_2$  solution + 2 drops  $\text{NaHSnO}_2$  solution (mix immediately before use equal volumes of 25% NaOH and a solution of 5 g.  $\text{SnCl}_2$  in 5 ml. conc. HCl diluted to 100 ml. with  $\text{H}_2\text{O}$ ). Black to brown precipitate. Run blank. Sensitivity: 0.01  $\mu\text{g}$ . Interference: Au, Ag, Pt, Hg(ignition), Cu(KCN), Te.

✓ **Cadmium.** *Di-p-nitrophenylcarbazine (SP)*. 1 drop test solution + 1 drop 10% NaOH + 1 drop 10% KCN. Mix. Add 1 drop 0.1% alcoholic reagent solution + 2 drops 40% HCHO. Stir. Blue-green precipitate or color. Sensitivity: 0.8  $\mu\text{g}$ . Interfere: Co, Pt, (Te and Fe may). Do not interfere: Hg(II), Cu, Pb, Bi.

✓ **Calcium.** *Glyoxal bis(2-hydroxyanil) (TT)*. 1 drop neutral or slightly acidic test solution + 4 drops saturated alcoholic solution of reagent \* + 1 drop solution (10 g. NaCN + 10 g. NaOH in 100 ml.  $\text{H}_2\text{O}$ ). Extract with  $\text{CHCl}_3$ . Red  $\text{CHCl}_3$  layer. Sensitivity: 0.25  $\mu\text{g}$ . Interference: Ba and Sr (both, 1 drop 10%  $\text{Na}_2\text{CO}_3$  after NaCN-NaOH solution).

✓ **Cerium.** *H<sub>2</sub>O<sub>2</sub> + NH<sub>3</sub> (C)*. 1 drop test solution + 1 drop 3%  $\text{H}_2\text{O}_2$  + 1 drop dil.  $\text{NH}_3$ . Heat gently. Yellow color or precipitate. Sensitivity: 0.4  $\mu\text{g}$ . Interfere: Fe(III) (tartrate). Do not interfere: rare earths.

✓ **Cesium.** *KBI<sub>4</sub> (FP)*. 1 drop test solution + 1 drop reagent (dissolve 1 g.  $\text{Bi}_2\text{O}_3$  by boiling in a saturated aqueous solution of 5 g. KI, and add in small portions 25 ml. glacial HAc). Run blank. Orange or yellow color. Sensitivity: 0.7  $\mu\text{g}$ . Interfere: Tl(I) and ions precipitated with KI (prior precipitation with KI). Do not interfere: Alkali metals.

✓ **Chromium (III).** *Diphenylcarbazine (SP)*. 1 drop test solution + 1 drop saturated  $\text{K}_2\text{S}_2\text{O}_8$  solution + 1 drop 2%  $\text{AgNO}_3$ . After 2-3 minutes, add 1 drop conc.  $\text{H}_2\text{SO}_4$  and 1 drop 1% alcoholic reagent solution. Violet to red color. Sensitivity: 0.8  $\mu\text{g}$ . Interference: Mn(II) ( $\text{NaN}_3$ ), Hg(II) ( $\text{Cl}^-$ ),  $\text{MoO}_4^{=}$  ( $\text{H}_2\text{C}_2\text{O}_4$ ),  $\text{VO}_3^-$ , Au(III).

\* Reagent. Dissolve 4.4 g. freshly sublimed o-aminophenol in 1 liter  $\text{H}_2\text{O}$  at  $80^\circ$  + 3.0 g. 40% glyoxal in  $\text{H}_2\text{O}$ . Let stand 30 min. at  $80^\circ\text{C}$ ., and then 12 hours in a refrigerator. Filter wash with  $\text{H}_2\text{O}$ , and recrystallize from MeOH.

**Chromium (VI).** *Chromotropic Acid*(SP). 1 drop test solution + 1 drop saturated reagent solution + 1 drop 7.5 N  $\text{HNO}_3$ . If Cr(III), make test solution slightly basic and add  $\text{Na}_2\text{O}_2$ . Destroy excess  $\text{Na}_2\text{O}_2$  with  $\text{KNO}_3$  and heat. Acidify and make test. Brownish-red color. Sensitivity: 2.5  $\mu\text{g}$ . Reaction is selective.

**Cobalt.** *1-Nitroso-2-naphthol*(FP). 1 drop neutral or slightly acidic test solution + 1 drop reagent (1 g. reagent in 50 ml. glacial  $\text{HAc}$  diluted to 1 liter with  $\text{H}_2\text{O}$ ). Brown stain. Sensitivity: 0.05  $\mu\text{g}$ . Interference:  $\text{Fe(III)(PO}_4^{3-})$ ,  $\text{UO}_2^{++}(\text{PO}_4^{3-})$ , Pd, Cu(KI +  $\text{Na}_2\text{SO}_3$ ).

**Cobalt.**  $\text{NH}_4\text{SCN}$ (SP). 1 drop test solution + 5 drops saturated reagent in acetone. Green to blue color. Sensitivity: 0.5  $\mu\text{g}$ . Interference:  $\text{Fe(III)(NaF)}$ ,  $\text{Cu(Na}_2\text{SO)}_2$ ,  $\text{VO}^{++}$ ,  $\text{CN}^-$ ,  $\text{C}_2\text{O}_4^{--}$ ,  $\text{Fe(CN)}_6^{3-}$ .

**Copper.** *Cuprouin*(SP). 1 drop test solution + 3-4 crystals  $\text{NH}_4\text{OH}\cdot\text{HCl}$  + 1 drop saturated alcoholic solution of reagent. Extract with isoAmOH if colored ions interfere. Pink to purple color. Sensitivity: 0.05  $\mu\text{g}$ . Interference:  $\text{IO}_4^-$ .

**Copper.** *Rubeanic Acid* (FP). 1 drop 20% malonic acid + 1 drop test solution + 1 drop saturated reagent in MeOH. Green-black spot. Sensitivity: 0.025  $\mu\text{g}$ . Interference: Au(III) (gold spot), Ag(NaCl).

**Gallium.** *Rhodamine B*(TT). 1 drop test solution (6 N in  $\text{HCl}$ ) + 3 drops 0.2% reagent in 6 N  $\text{HCl}$  + 3-5 drops benzene. Mix. Run blank. Red benzene layer (orange-red fluorescence in ultraviolet light). Sensitivity: 0.5  $\mu\text{g}$ . Interference: Hg(II), Sb, Au(III), Fe(III),  $\text{TeO}_3^{--}$ ,  $\text{SCN}^-$ ,  $\text{BrO}_3^-$ ,  $\text{IO}_3^-$ ,  $\text{MnO}_4^-$ ,  $\text{CrO}_4^{--}$ .

**Germanium.** *Mannitol*(TT). 1 drop slightly acidic test solution (germanate) + 1 drop phenolphthalein + 0.01 N  $\text{NaOH}$  to red color. Add solid mannitol. Red color fades or disappears. Sensitivity: 2.5  $\mu\text{g}$ . In the absence of B, specific for Ge. Do not interfere: As(III), Sb, Sn, Te.

**Gold.** *p-Dimethylaminobenzalrhodanine*(FP). 1 drop neutral or slightly acidic test solution on filter paper (S & S No. 601) impregnated with saturated alcoholic solution of reagent and dried. Violet spot. Sensitivity: 0.1  $\mu\text{g}$ . Interference: Ag( $\text{Cl}^-$ ), Hg( $\text{Cl}^-$ ), Pd(dimethylglyoxime +  $\text{H}^+$  and filter — use filtrate).

**Indium.** *Alizarin*(FP). 1 drop test solution (slightly acidic or neutral) on filter paper impregnated with saturated alcoholic solution of reagent and dried. Hold over conc.  $\text{NH}_3$  and dip in saturated aqueous  $\text{H}_3\text{BO}_3$ . Red spot. Sensitivity: 0.05  $\mu\text{g}$ . Interference: Be, Zr, Th, Al( $\text{F}^-$ ), Cr( $\text{NaOH}$ ),  $\text{Fe(Na}_2\text{S}_2\text{O}_3 + \text{KCN})$ , Zn( $\text{CN}^-$ ), Ni( $\text{CN}^-$ ), Co( $\text{CN}^-$ ), Mn( $\text{CN}^-$ ), most ions precipitated with  $\text{H}_2\text{S}$ .

**Iridium.** *Leucomalachite green*(TT). 2-3 ml. test solution + {2-3 drops 1% reagent in 2 N  $\text{HAc}$  +  $\text{CHCl}_3$ . Shake. Green color with  $\text{IrCl}_6^{--}$ . Dilution limit: 1:10<sup>4</sup>. Interfere: Au, Ru, Pd(IV), Fe(III). Do not interfere:  $\text{PtCl}_6^{--}$ ,  $\text{RhCl}_6^{--}$ , Pt(II), Os(IV).

**Iron(II).** *2,2'-Dipyridyl* (or *1,10-phenanthroline*)(SP or FP). 1 drop slightly acidic test solution + 1 drop 2% alcoholic reagent solution on spot plate, or 1 drop test solution on filter paper (S & S No. 589) impregnated with 2% alcoholic reagent solution and dried. Red to pink color. Sensitivity: 0.25  $\mu\text{g}$ . Fe(III) is detected by prior reduction with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  or  $\text{SnCl}_2$ . The reaction is selective.

**Iron(III).**  $\text{K}_4\text{Fe(CN)}_6$ (FP or SP). 1 drop slightly acidic test solution + 1 drop 1% reagent solution. Blue stain or precipitate. Sensitivity: 0.5  $\mu\text{g}$ . Interference:  $\text{F}^-$ ,  $\text{C}_2\text{O}_4^{--}$ ,  $\text{PO}_4^{3-}$ , and cations forming colored ferrocyanides may.

**Lead.** *Dithione*(TT). 1 drop test solution + 2 drops 5 N  $\text{KCN}$  + 1 drop conc.  $\text{NH}_4\text{OH}$  + 4-5 drops saturated solution of reagent in  $\text{CCl}_4$ . Red  $\text{CCl}_4$  layer. Sensitivity: 0.05  $\mu\text{g}$ . Interference: Sn(II,IV), Fe(III),  $\text{PO}_4^{3-}$ .

**Lithium.**  $\text{KIO}_4 + \text{FeCl}_3 + \text{KOH}$ (TT). 1 drop neutral or basic test solution + 1 drop saturated NaCl + 2 drops reagent (dissolve 2 g.  $\text{KIO}_4$  in 10 ml. freshly prepared 2 N  $\text{KOH}$ . Dilute to 50 ml. and mix with 3 ml. 10%  $\text{FeCl}_3$  and dilute to 100 ml. with 2 N

KOH). Prepare blank with  $H_2O$ . Dip both tubes in  $H_2O$  at  $45-50^\circ C$ . for 15-20 seconds. Yellow-white turbidity (blank clear). Sensitivity:  $0.1 \mu g$ . Interference:  $NH_4^+$  (heat + KOH or ignite solid), bivalent metals (oxine in KOH—use filtrate).

**Magnesium.** *Magneson*(SP). 1 drop neutral or slightly acidic test solution + 1 drop 0.1% reagent in 1:1 EtOH + 1-2 drops 0.1 N KOH. Blue color or precipitate. Sensitivity:  $0.5 \mu g$ . Interfere: Fe, Cr, Al, Sn (all precipitated with solid  $NaNO_2$ ), Ni, Co, Cd (all with  $CN^-$ ), Mn( $S^{=}$ ),  $NH_4$  salts (heat). Do not interfere: Ca, Ba, Sr.

**Manganese.**  $(NH_4)_2S_2O_8 + AgNO_3$ (C or TT). 1 drop test solution + 1 drop conc.  $H_2SO_4$ . Mix. Add 1 drop 0.1%  $AgNO_3$  + few mg.  $(NH_4)_2S_2O_8$ . Heat gently. Red-violet color. Sensitivity:  $0.1 \mu g$ . Interference: Cr(III), (see  $MnO_4^-$  test), halides.

**Mercury(I) and (II).** *Diphenylcarbazone*(FP). 1 drop test solution (0.2 N  $HNO_3$ ) + 1 drop 1% alcoholic reagent solution. Violet-blue precipitate. Sensitivity:  $0.5 \mu g$ . Interference: halides and  $CN^-$ .

**Mercury(I) and (II).**  $SnCl_2 + Aniline$ (FP). 1 drop test solution + 1 drop 5%  $SnCl_2$  in 10 N HCl + 1 drop pure aniline. Black to brown stain. Sensitivity:  $1 \mu g$ . Interference: large amounts Ag, Au, Mo.

**Molybdenum.** *Methylene blue*(TT). 1 drop slightly acidic test solution ( $MoO_4^{=}$ ) + 4 drops 0.0012% reagent solution + 20-30 mg. solid  $N_2H_4 \cdot H_2SO_4$ . Prepare blank. Place both tubes in boiling  $H_2O$ . With  $>0.5 \mu g$  Mo, color discharged in 3 minutes; with  $<0.5 \mu g$  Mo, in 10 minutes. Sensitivity:  $0.012 \mu g$ . Interference: Colored ions, W( $F^-$ ), Sn(II),  $NO_3^-$ ,  $S^{=}$ ,  $S_2O_3^{=}$ , Se. With many cations, boil with  $Na_2CO_3$  and use filtrate.

**Nickel.** *Dimethylglyoxime*(SP). 2-3 drops test solution +  $NH_3$  until basic. Filter. To 1 drop filtrate, add 1 drop saturated alcoholic solution of reagent. Pink to red precipitate. Sensitivity:  $0.2 \mu g$ . Interference: Fe(II) ( $H_2O_2$ ), Fe(III)( $F^-$ ), Cu( $HSO_3^- + SCN^-$ ), Co + Ni( $CN^- + HCHO$ ), Co, Cu, Mn (all  $H_2O_2 + Na_2CO_3$ ), Pd (may).

**Niobium.**  $KSCN + Zn$ (TT). Crystals of KSCN + 1 ml. test solution (niobate) + Zn powder + 5 drops conc. HCl. Yellow. Run blank. Dilution limit: 1:20,000. Do not interfere:  $Ta_2O_5$ , Ti(IV),  $WO_4^{=}$ .

**Osmium.**  $KClO_3 + KI$ (SP). 1 drop reagent (1 g.  $KClO_3$  + 1 g. KI + 100 ml.  $H_2O$ ) + 1 drop 1:1000  $H_2SO_4$  + 1 drop 1% starch solution + 1 drop neutral test solution. Blue color. Run blank. Sensitivity:  $0.005 \mu g$   $OsO_4$ . Interference: Ru, colored ions, oxidizing agents. Specific for Os if  $OsO_4$  is volatilized from acidic test solution and collected in 1 drop  $H_2O$ ( $0.01 \mu g$ ).

**Palladium(II).** *Dimethylglyoxime*(FP). 1 drop slightly acidic test solution on test paper. (Dip filter paper in saturated alcoholic solution of reagent. Dry, and dip in slightly  $NH_3$  5% Ni( $NO_3$ ) $_2$  solution. Wash with  $H_2O$ , dip in EtOH and dry.) Dry spot + dil. HCl + cold  $H_2O$ . Red color disappears except at test spot. Sensitivity:  $0.25 \mu g$ . Interference: Hg(I),  $CN^-$ ,  $S_2O_3^{=}$ ,  $Fe(CN)_6^{3-}$ .

**Platinum.** *p-Nitrosodimethylaniline*(TT). 4 drops dil. HAc + 2 drops test solution + 4 drops 0.05% reagent in 60% EtOH. Heat in boiling  $H_2O$  for 5 minutes. Pink color. Sensitivity:  $2.5 \mu g$ . Interference: Au(III), Rh(III), Pd(II), Ru(III), Ce(IV),  $SCN^-$ ,  $Fe(CN)_6^{3-}$ ,  $TeO_3^{=}$ ,  $BrO_3^-$ .

**Potassium.**  $Na_3[Co(NO_2)_6]$ (S). 1 drop test solution + 1 drop EtOH + 1 drop reagent solution (0.5 g. reagent + 3 ml.  $H_2O$ ). Yellow crystals. View against black background. Sensitivity:  $4 \mu g$ . Do not interfere: Na, Rb, Cs,  $NH_4^+$ .

**Rhenium.** *Dimethylglyoxime* +  $SnCl_2$ (SP). 1 drop test solution ( $ReO_4^-$ ) + 1 drop saturated alcoholic dimethylglyoxime + crystals of  $SnCl_2$  + 1 drop conc. HCl. Brown to reddish-brown color. Sensitivity:  $2 \mu g$ . Interference:  $MoO_4^{=}$ , Pt(IV), Au(III),  $SeO_3^{=}$ ,  $SeO_4^{=}$ .

**Rhodium.** *p*-Nitrosodiphenylamine(TT). 3-5 drops slightly acidic test solution + 4 drops 0.05% reagent in 1:1 EtOH. Heat in boiling H<sub>2</sub>O for 5 minutes. Orange-red solution. Sensitivity: 0.5  $\mu$ g. Interference: Pt(IV), Os(III), Ce(IV), Fe(III), Zr(IV), SCN<sup>-</sup>, NO<sub>2</sub><sup>-</sup>.

**Rubidium.** *AuBr<sub>3</sub>-AgBr(M)*. Evaporate on slide 1 drop test solution. To residue add 1 drop 4.5% AuBr<sub>3</sub> solution in 40% HBr and 1 drop 0.8% AgBr in 40% HBr. Let stand a few minutes. Red, prismatic needles. Sensitivity: 0.5  $\mu$ g. Interference: Cs, Sb, Sn, Ru, Rh, Pt.

**Ruthenium.** *Rubeanic Acid(TT)*. 1 drop HCl test solution + 1-2 drops 0.2% reagent in glacial HAc. Heat gently. Blue color. Sensitivity: 0.2  $\mu$ g. Interference: Pd and Pt give red precipitates (blue color may be observed after filtering or centrifuging). Os does not react.

**Scandium.** *Cochineal(TT)*. 5 ml. test solution + 2-3 drops tincture cochineal + few drops 2 N NaOH to a purple color. Heat gently + 10 drops glacial HAc. Dark blue precipitate. Dilution limit: 1:50,000. Interference: Zr(IV), Ti(IV), UO<sub>2</sub><sup>++</sup>, F<sup>-</sup>. Also Ag, Hg, Cu, Sn, Au, V (all removed with H<sub>2</sub>S).

**Selenium.** *Diphenylbenzidine(SP)*. 1 drop test solution + 1 drop 5% NaF + 1 drop 2.5% reagent solution + 1 drop dilute HCl. Yellow color or precipitate. Sensitivity: 2.5  $\mu$ g. Interference: Au(III), Ce(IV), VO<sub>3</sub><sup>-</sup>, Ru(III), Pt(IV), oxidizing anions.

**Selenium.** *NaHSO<sub>3</sub>(TT)*. 1 ml. test solution + crystals of NaHSO<sub>3</sub> + 1 ml. conc. H<sub>2</sub>SO<sub>4</sub>. Heat to boiling 1 minute. Cool. Red color or precipitate. Sensitivity: 6  $\mu$ g. Interference: Sn(II). Do not interfere: As(III), Sn(IV), Ge(IV), Te.

**Silver.** *(NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> + HCl(SP)*. Use adjacent depressions on spot plate. To each add 3 drops reagent solution (0.25% reagent in 1% HNO<sub>3</sub>) + 2 drops dilute HCl. To one add 1 drop test solution, and to the other 1 drop H<sub>2</sub>O. Reagent decolorizes more rapidly with Ag. Sensitivity: 0.05  $\mu$ g. Interference: Mn, reducing agents, especially Fe(II) and Sn(II).

**Sodium.** *Zinc uranyl acetate(Black SP)*. Make test solution as nearly neutral as possible. 1 drop neutral test solution + 8 drops reagent.\* Stir. Yellow precipitate. Sensitivity: 12.5  $\mu$ g. Specific for Na. Large amounts of Li and K may precipitate.

**Strontium.** *Na Rhodizonate(FP)*. 1 drop test solution on filter paper impregnated with saturated aqueous K<sub>2</sub>CrO<sub>4</sub> solution and dried. Let stand 1 minute. Add 1 drop 0.2% reagent solution. Red brown spot. Sensitivity: 4  $\mu$ g. Ba does not interfere.

**Tantalum.** *Methylene blue(TT)*. 1 ml. test solution (TaF<sub>5</sub> or TaF<sub>7</sub><sup>-</sup>) + 1 ml. saturated aqueous reagent. Blue precipitate. Run blank. Dilution limit: 1:10,000. Do not interfere: Nb, Ti(IV), and low concentrations of Sb, Sn, Mo, W, V, Al.

**Tellurium.** *SnCl<sub>2</sub> + NaOH(SP)*. 1 drop reagent (5 g. SnCl<sub>2</sub> + 5 ml. conc. HCl diluted to 100 ml.) + 1 drop 25% NaOH + 1 drop basic test solution (Na<sub>2</sub>CO<sub>3</sub> extract). Black precipitate or gray color. Sensitivity: 0.6  $\mu$ g. Interference: Ag, Hg, Cu, Bi, As(III), Sb(III), Sn(IV), Mo(VI). Se does not react.

**Thallium(I).** *KI(WG)*. 1 drop slightly acidic test solution + 1 drop 10% KI on watch glass (black background). After precipitate form + 1-2 drops 2% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Yellow precipitate insoluble in Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> indicates Tl. Sensitivity: 0.6  $\mu$ g. Interference: Hg(excess KI), Pb(Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>), Ag(Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>).

**Thorium.** *KIO<sub>4</sub>(TT)*. 5 ml. slightly acidic test solution + 5 drops 7.5 N HNO<sub>3</sub> + few drops saturated aqueous solution of reagent. White precipitate. Dilution limit: 1:250,000. Interference: Ag, Hg, Sn, Ti, Zr. Do not interfere: rare earths.

\* *Reagent (A)*. Dissolve 10 g. uranyl acetate by warming in 6 g. 30% HAc and dilute to 50 ml. *Reagent (B)*. Stir 30 g. zinc acetate with 3 g. 30% HAc and dilute to 50 ml. Mix (A) and (B). Add trace NaCl. Let stand 24 hours and filter.

**Tin.**  $Zn + HCl(C)$ . 5 drops test solution + 5 ml. conc. HCl + piece Zn. Dip micro-test tube filled with cold  $H_2O$  in mixture, then in reducing flame of Bunsen burner. Blue luminescence. Dilution limit: 1:5000. Not sensitivity but selective. Interference: Nb, (Au may).

**Titanium.** *Chromotropic Acid(SP)*. 1 drop test solution + 1 drop 5% reagent solution. Red-brown color. Sensitivity: 3  $\mu g$ . Interference:  $Fe(III)(SnCl_2)$ ,  $UO_2^{++}(SnCl_2)$ ,  $PO_4^{3-}$ ,  $F^-$ ,  $SeO_3^{2-}$ ,  $C_2O_4^{2-}$ .

**Titanium.** *Chromotropic Acid(SP)*. 1 drop  $H_2SO_4$  test solution + 5 drops reagent (0.02 g. reagent in 20 ml. conc.  $H_2SO_4$ ). Violet color. Sensitivity: 0.1  $\mu g$ . Interference:  $NO_3^-$ , oxidizing agents (fume with conc.  $H_2SO_4$ ).

**Titanium.**  $H_2O_2(TT)$ . 1 ml. test solution + 3-4 drops 4 N  $H_2SO_4$  + 1 drop 3%  $H_2O_2$ . Orange-yellow color. Color disappears with solid  $NH_4F$  if caused by Ti. Dilution limit: 1:100,000. Interference:  $Fe(III)(H_3PO_4)$ ,  $F^-(BeCl_2)$ ,  $CrO_4^{2-}$ ,  $VO_3^-$ ,  $MoO_4^{2-}$ ,  $Au(III)$ ,  $Pt(IV)$ ,  $UO_2^{++}$  (with last 3 ions, run blank).

**Tungsten.**  $SnCl_2(FP)$ . 1 drop conc. HCl + 1 drop test solution 1 drop 10% KSCN + 1 drop freshly prepared 20%  $SnCl_2$  in conc. HCl. Bluish-green spot. Sensitivity: 5  $\mu g$ . Interfere:  $Au(III)$ ,  $Ru(III)$ ,  $F^-$ ,  $C_2O_4^{2-}$ ,  $Te$ ,  $Se$ . Do not interfere: Nb, Ta.

**Uranium.**  $K_4Fe(CN)_6(FP)$ . 1 drop slightly acidic test solution + 1 drop 3% reagent solution. Brown stain. Sensitivity: 1  $\mu g$ . Interference:  $Fe(III)$ ,  $Cu(II)$  (both with  $KI + H^+ + Na_2S_2O_3$ ).

**Uranium.** *Oxine(FP)*. 1 drop slightly acidic test solution + 1 drop 5% alcoholic reagent solution. Expose to  $NH_3$  gas. Clear brown stain. Sensitivity: 3  $\mu g$ . Interference: Positive in presence of rare earth and principal elements in U ores, except Fe.  $Sb(V)$ ,  $Fe$ ,  $Ce(IV)$ ,  $F^-$ ,  $PO_4^{3-}$ , aliphatic hydroxy acids (Fe cannot be masked by latter).

**Vanadium.** *Oxine(TT)*. 2 drops test solution + 3 drops saturated solution of reagent in glacial HAc. Adjust pH to 4-6 + 6-7 drops isoAmOH. Shake. Red alcoholic layer. Sensitivity: 2.5  $\mu g$ . Interference:  $MnO_4^-$ ,  $H_2O_2$ ,  $Cu$ ,  $Au$ ,  $Fe(NaOH)$ ,  $Ru$ ,  $Sn(II)$  (all may).  $Mo$ ,  $W$ ,  $Ti(NaOH + HAc + BaAc_2)$ .

**Zinc.** *Dithizone(TT)*. 1 drop test solution (pH 4.0-5.5) + 2 drops 10%  $Na_2S_2O_3$  + 1 drop 2 M  $NH_4CN$  + 5 drops 0.002% reagent solution in  $CCl_4$ . Red  $CCl_4$  layer. Sensitivity: 0.06  $\mu g$ . Interference:  $Cd$ ,  $Sn(II)$ ,  $Pb$ ,  $As(III)$ .

**Zirconium.** *AlizarinS(SP)*. 1 drop slightly acidic test solution + 1 drop 1% reagent solution + 1 drop conc. HCl. Red ppt. Sensitivity: 1.0  $\mu g$ . Interference:  $F^-$ .

### Detection of the Anions

**Acetate.**  $La(NO_3)_3 + I_2(SP)$ . 1 drop test solution + 1 drop 5%  $La(NO_3)_3$  + 1 drop 0.01 N  $I_2$  in  $KI$  + 1 drop 1 N  $NH_3$ . Blue color. Sensitivity: 15  $\mu g$ . Propionate gives same reaction. Formate, butyrate, valerate, lactate do not interfere.

**Arsenate.** See Arsenic.

**Arsenite.** See Arsenic.

**Borate.** *Turmeric(FP)*. 1 drop slightly HCl test solution on filter paper impregnated with reagent (heat 20 g. reagent with 5 ml. EtOH, filter and dilute with 50 ml.  $H_2O$ ) and dried. Dry at 100°C. Add 1 drop 1% NaOH. Red-brown which turns greenish-black with NaOH. Sensitivity: 2.5  $\mu g$ . Interference:  $Zr(IV)$ .

**Bromate.**  $MnSO_4 + H_2SO_4(TT)$ . 1 drop test solution + 1 drop 2%  $MnSO_4$  acidified with  $H_2SO_4$ . Heat 2-3 minutes on water bath. Cool and add 2-3 drops HAc—benzidine reagent (0.05 g. benzidine in 10 ml. HAc, diluted to 100 ml. and filtered) + few crystals NaAc. Blue color. Sensitivity: 20  $\mu g$   $KBrO_3$ . Do not interfere:  $ClO_3^-$  and  $IO_3^-$ . Not selective.



**Bromide.** *Fluorescein*(FP). In test tube place 1 drop test solution + solid  $\text{PbO}_2$  + 5 drops 2 *N* HAc. Over test tube place filter paper impregnated with saturated solution of dye in 1:1 EtOH. Heat. Red color. Sensitivity: 2  $\mu\text{g}$ . Interference:  $\text{I}^-$ , reducing ions as  $\text{S}^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$ .

**Bromine (and Hypobromite).** *Fluorescein*(FP). 1 ml. test solution in test tube covered with filter paper (negative  $\text{I}_2$  test) impregnated with 0.1% reagent in slightly basic 1:1 EtOH. Pink color. Sensitivity: 1  $\mu\text{g}$ . Interference:  $\text{S}^{2-}$ (HAc),  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$ .

**Carbonate.**  $\text{Na}_2\text{CO}_3$  + *Phenolphthalein*(TT). 1-2 drops test solution (or solid) + 3 drops 2 *N*  $\text{H}_2\text{SO}_4$ . Collect  $\text{CO}_2$  gas in 1 drop red reagent solution (1 ml. 0.1 *N*  $\text{Na}_2\text{CO}_3$  + 2 ml. 0.5% alcoholic phenolphthalein in 10 ml.  $\text{H}_2\text{O}$ .) Red color decolorized. Run blank. Sensitivity: 4  $\mu\text{g}$  (in 2 drops test solution). Interference:  $\text{CN}^-$ ( $\text{Ag}^+$ ),  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ (all  $\text{H}_2\text{O}_2$ ),  $\text{F}^-$ ( $\text{ZrCl}_4$ ),  $\text{NO}_2^-$ (aniline HCl),  $\text{Ac}^-$ .

**Chlorate.**  $\text{MnSO}_4$  +  $\text{H}_3\text{PO}_4$ (C). 1 drop test solution + 1 drop reagent solution (equal volumes saturated aqueous  $\text{MnSO}_4$  and syrupy  $\text{H}_3\text{PO}_4$ ). Heat and cool. Violet color. If color is inconclusive, add 1 drop 1% alcoholic diphenylcarbazine. Sensitivity: 0.05  $\mu\text{g}$ . Interference:  $\text{S}_2\text{O}_8^{2-}$ (evaporate with  $\text{H}_2\text{SO}_4$  +  $\text{AgNO}_3$ ),  $\text{IO}_4^-$ ,  $\text{ClO}^-$ ,  $\text{BrO}_3^-$ ,  $\text{IO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{Fe}(\text{CN})_6^{3-}$ .

**Chloride.**  $\text{As}_2\text{CrO}_7$  + *diphenylcarbazine*(SP). Evaporate test solution to dryness. Residue + solid  $\text{K}_2\text{Cr}_2\text{O}_7$  + 1 drop conc.  $\text{H}_2\text{SO}_4$ . Heat and collect vapor in 1 drop  $\text{H}_2\text{O}$  (avoid contact with reagent). To this drop on spot plate add 1 drop 1% alcoholic diphenylcarbazine + 1 drop 2 *N*  $\text{H}_2\text{SO}_4$ . Red to violet color. Dilution limit: 1:10,000. Interference:  $\text{Br}^-$ ,  $\text{BrO}^-$ ,  $\text{BrO}_3^-$ (all + phenol),  $\text{F}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ .

**Chlorine (and Hypochlorite).** *Aniline* + *Phenol*(TT). 1 ml. test solution + 5 drops 1 *N*  $\text{NaOH}$  + 0.5 ml. saturated aqueous aniline + 5 drops 5% aqueous phenol. Blue color. Sensitivity: 30  $\mu\text{g}$ . Interference:  $\text{Br}_2$ ,  $\text{BrO}^-$ (brown),  $\text{S}^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SCN}^-$ ,  $\text{Fe}(\text{CN})_6^{3-}$ ,  $\text{S}_2\text{O}_3^{2-}$ .

**Chromate.** *Diphenylcarbazine*(SP). 1 drop test solution + 1 drop conc.  $\text{H}_2\text{SO}_4$  (if  $\text{MnO}_4^-$  present, add  $\text{NaN}_3$  to decolorize) + 1 drop 1% alcoholic reagent solution. Blue-violet color. Sensitivity: 0.3  $\mu\text{g}$   $\text{K}_2\text{Cr}_2\text{O}_7$ . (See also Chromium.)

**Cyanide.**  $\text{CuAc}_2$  + *benzidine*(FP). Heat test solution slightly in test tube and add solid  $\text{NaHCO}_3$ . Collect gas on filter paper impregnated with 1 drop 3%  $\text{CuAc}_2$  solution and 1 drop 1% benzidine in 10% HAc. Blue color. Dilution limit: 1:20,000. Interference:  $\text{Cl}_2$ ,  $\text{Br}_2$ .

**Cyanide.**  $\text{CuS}$ (FP). Dip filter paper in  $\text{NH}_3$  solution of 1 g.  $\text{CuSO}_4$  per liter and dry. Immediately before use, expose to  $\text{H}_2\text{S}$ . To brown paper add 1 drop test solution. White spot. Sensitivity: 1.25  $\mu\text{g}$ . Test may be used in presence of ferro- and ferricyanide,  $\text{I}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SCN}^-$ .

**Ferricyanide.** *Benzidine acetate*(SP). 1 drop neutral test solution + 1 drop 2 *N* HAc saturated cold with benzidine. Blue color or precipitate. Sensitivity: 1  $\mu\text{g}$ . Interference: Many oxidizing agents. Useful only to detect ferricyanide in presence of ferrocyanide ( $\text{PbAc}_2$ ).

**Ferricyanide.**  $\text{FeSO}_4$ . Blue color or precipitate. Ferrocyanide interferes.

**Ferrocyanide.**  $\text{FeCl}_3$ (SP). 1 drop HCl test solution + 1 drop 1%  $\text{FeCl}_3$ . Blue color. Sensitivity: 1.3  $\mu\text{g}$ . Interference:  $\text{I}^-$ ,  $\text{SCN}^-$  (capillary separation on filter paper).

**Fluoride.** *Zr-Alizarin Lake*(SP). 1 drop test solution + 1 drop 0.1 % HCl + 1 drop reagent (mix equal volumes 0.17% alizarin S and 0.87%  $\text{Zr}(\text{NO}_3)_4$  and dilute 1:5 with  $\text{H}_2\text{O}$ ). Pink color, fades to yellow. Sensitivity: 0.1  $\mu\text{g}$ . Interference:  $\text{Ce}(\text{IV})$ ,  $\text{VO}_5^-$ , and large amounts  $\text{SO}_4^{2-}$ . Al, Ce(III), Be, Th, and large amounts Si and  $\text{S}^{2-}$  may interfere.

**Iodate.** *KSCN(FP)*. 1 drop 5% *KSCN* on starch paper + 1 drop acidic test solution. Blue color. Sensitivity: 4  $\mu\text{g}$   $\text{NaIO}_3$ .

**Iodide.** *Starch(SP)*. 1 drop acidic test solution + 1 drop starch solution + 1 drop 10%  $\text{KNO}_2$ . Blue color. Sensitivity: 2.5  $\mu\text{g}$ . Interference:  $\text{CN}^-$  ( $\text{H}^+$  + heat).

**Iodine.** *Starch(SP)*. 1 drop test solution + 1 drop 1% soluble starch solution. Blue color. Sensitivity: 0.3  $\mu\text{g}$ . Interference:  $\text{Br}_2$ ,  $\text{Cl}_2$ ,  $\text{CN}^-$  ( $\text{NaHCO}_3$  + heat).

**Molybdate.** See Molybdenum.

**Nitrate.** *Zn + 1-naphthylamine + sulfanilic acid(SP)*. 1 drop neutral or *HAc* test solution + 1 drop sulfanilic acid solution (1 g. reagent in 100 ml. 30% *HAc* with heat) + 1 drop 1-naphthylamine solution (boil 0.03 g. reagent with 70 ml.  $\text{H}_2\text{O}$  and decant clear solution into 30 ml. glacial *HAc*) + few mg. *Zn* dust. Red color. Sensitivity: 0.05  $\mu\text{g}$ . Interference:  $\text{NO}_2^-$  ( $\text{NaN}_3$  +  $\text{H}^+$  and boil).

**Nitrite.** *1-Naphthylamine + sulfanilic acid(SP)*. 1 drop neutral or *HAc* test solution + 1 drop sulfanilic acid reagent (see Nitrate) + 1 drop 1-naphthylamine reagent (see Nitrate). Red color. Sensitivity: 0.01  $\mu\text{g}$ . Interference: strong oxidizing agents, *Fe*(III) (tartrate).

**Periodate.** *Tetabase + MnSO<sub>4</sub>(SP)*. 1 drop test solution + 1 drop 10%  $\text{MnCl}_2$  solution + 1 drop saturated tetabase in 2 *N HAc*. Blue color. Sensitivity: 0.5  $\mu\text{g}$ . Interference:  $\text{S}_2\text{O}_8^{2-}$  (heat with  $\text{AgNO}_3$ ). Not selective, but  $\text{ClO}_3^-$ ,  $\text{BrO}_3^-$ , and  $\text{IO}_3^-$  do not interfere. (See also, Chlorate).

**Permanganate.** Purple color.

**Perrhenate.** See Rhenium.

**Persulfate.** *Benzidine(SP)*. 1 drop neutral or slightly acidic test solution + 1 drop 2% reagent in dilute *HAc*. Blue color. Sensitivity: 1  $\mu\text{g}$ . Interfere:  $\text{CrO}_4^{2-}$ ,  $\text{MnO}_4^-$ ,  $\text{Fe}(\text{CN})_6^{3-}$ , hypohalites. Do not interfere: alkali peroxides, perborates, and  $\text{H}_2\text{O}_2$ ,  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{BrO}_3^-$ ,  $\text{IO}_3^-$ ,  $\text{NO}_3^-$ .

**Phosphate.** *(NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> + Benzidine(FP)*. 1 drop acidic test solution + 1 drop molybdate solution (5 g.  $(\text{NH}_4)_2\text{MoO}_4$  in 100 ml.  $\text{H}_2\text{O}$  added to 35 ml. 6*N HNO*<sub>3</sub>). + 1 drop benzidine solution (0.05 g. benzidine in 10 ml. glacial *HAc* and diluted to 100 ml. with  $\text{H}_2\text{O}$ ). Expose to  $\text{NH}_3$  gas. Blue color. Sensitivity: 1.5  $\mu\text{g}$   $\text{P}_2\text{O}_5$ . Interference:  $\text{SiO}_3^{2-}$  (*HCl* or tartaric acid),  $\text{AsO}_4^{3-}$  ( $\text{H}_2\text{S}$  or tartaric acid),  $\text{GeO}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{F}^-$  ( $\text{Be}^{++}$ ).

**Selenate.** See Selenium.

**Selenite.** See Selenium.

**Silicate.** *(NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> + SnCl<sub>2</sub>(SP)*. Solid sample + *NaF* + 2-3 drops conc.  $\text{H}_2\text{SO}_4$  in platinum crucible. Warm and collect  $\text{SiF}_4$  in 1 drop 2 *N NaOH* (freshly prepared). Add 2 drops 10%  $(\text{NH}_4)_2\text{MoO}_4$  and acidify with 4 *N HAc*. Add 3 drops 5%  $\text{SnCl}_2$  in 2.5*N HCl*. Add excess *NaOH* (freshly prepared) to dissolve  $\text{Sn}(\text{OH})_2$ . Blue color. Dilution limit: 1:10,000. Only  $\text{H}_3\text{BO}_3$  interferes. Remove by heating with *MeOH*.

**Sulfate.** *BaCl<sub>2</sub> + KMnO<sub>4</sub>(TT)*. 1 drop test solution + 1 drop 1%  $\text{KMnO}_4$  + 1 drop 1%  $\text{BaCl}_2$  + 2-3 drops  $\text{H}_2\text{O}_2$  (or oxalic acid) to decolorize solution. Deep purple precipitate. Sensitivity: 3  $\mu\text{g}$ . Interference:  $\text{ClO}^-$ ,  $\text{CN}^-$ ,  $\text{CNO}^-$ ,  $\text{SCN}^-$ ,  $\text{Fe}(\text{CN})_6^{3-}$ ,  $\text{Fe}(\text{CN})_6^{4-}$ . Precipitation of *Ba* salts prevented by *HAc*.

**Sulfide.** *NaN<sub>3</sub> + I<sub>2</sub>(WG)*. 1 drop test solution + 1 drop reagent (3 g.  $\text{NaN}_3$  in 100 ml. 0.1 *N I*<sub>2</sub>). Immediate evolution of tiny bubbles of gas. Run blank. Sensitivity: 0.3  $\mu\text{g}$ . Interference:  $\text{SCN}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{Se}^{2-}$ ,  $\text{Te}^{2-}$ .

**Sulfide.** *Nitroprusside(SP)*. 1 drop basic test solution + 1 drop 1% aqueous sodium nitroprusside solution. Purplish-red color. Sensitivity: 1  $\mu\text{g}$ . Selective test.  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_4^{2-}$  do not interfere.

**Sulfite.** *Nitroprusside (SP).* 1 drop saturated  $\text{Zn}(\text{NO}_3)_2$  + 1 drop 1 *N*  $\text{K}_4\text{Fe}(\text{CN})_6$  + 1 drop 1% aqueous sodium nitroprusside solution + 1 drop neutral test solution. White precipitate turns red. Sensitivity: 3.2  $\mu\text{g}$ . Interference:  $\text{S}^-$  in basic solution, violet color.  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_7^{2-}$  do not interfere.

**Tellurate.** See Tellurium.

**Tellurite.** See Tellurium.

**Thiocyanate.**  *$\text{FeCl}_3$  (TT).* 0.1 ml. test solution (acidified with 2 *N*  $\text{HCl}$ ) + 1 drop 1%  $\text{FeCl}_3$ . Red color. Sensitivity: 1  $\mu\text{g}$ . Interference: with  $\text{F}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{C}_2\text{O}_4^{2-}$ , tartrate, and citrate, use excess  $\text{FeCl}_3$ .  $\text{I}^-$ ,  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{Fe}(\text{CN})_6^{4-}$  (both of latter,  $\text{CdSO}_4$ ).

**Thiosulfate.**  $\text{NaN}_3$  +  $\text{I}_2$  (same as  $\text{S}^-$  test). Interference:  $\text{S}^-$ ,  $\text{SCN}^-$ ,  $\text{Te}^-$ ,  $\text{Se}^-$ .

**Tungstate.** See Tungsten.

**Vanadate.** See Vanadium.

# ***DIVISION OF THE ELEMENTS INTO ANALYTICAL GROUPS***

One of the oldest and most useful of the methods used to separate ions as a preliminary to their identification by qualitative tests is based on the division of the elements into analytical groups. The scheme in which hydrogen sulfide is used as a precipitant is perhaps the best known and is in many ways the most useful of the various methods that have been proposed. Using the group reagents of this scheme, a large number of highly important and useful separations can be effected.

The analytical groups and the elements of which they are composed are as follows:

- I. *The Hydrochloric Acid Group*  
Lead, mercury(I), silver, thallium(I).
- II. *The Hydrogen Sulfide Group*  
Antimony, arsenic, bismuth, cadmium, copper, germanium, gold, iridium, lead, mercury, molybdenum, osmium, palladium, platinum, rhenium, rhodium, ruthenium, selenium, silver, tellurium, tin. (Partially: thallium.)
  - A. *Elements whose Sulfides are Insoluble in Acids and in Solutions of Alkali Sulfides:* Bismuth, cadmium, copper, lead, mercury, silver. (Entirely or partially: osmium, palladium, rhodium, ruthenium.)
  - B. *Elements whose Sulfides are Insoluble in Acids but are Soluble in Solutions of Alkali Sulfides:* Antimony, arsenic, germanium, molybdenum, rhenium, selenium, tellurium, tin. (Entirely or partially: gold, iridium, platinum.)
- III. *The Ammonium Sulfide Group*  
Aluminum, beryllium, chromium, cobalt, gallium, indium, iron, manganese, nickel, niobium, rare earths, scandium, tantalum, thallium, thorium, titanium, uranium, vanadium, zinc, zirconium.
  - A. *Elements whose Sulfides are Soluble in Acids:* Cobalt, gallium, indium, iron, manganese, nickel, thallium, uranium, vanadium, zinc.
  - B. *Elements that Form Hydroxides or Basic Compounds:* Aluminum, beryllium, chromium, niobium, rare earths, scandium, tantalum, thorium, titanium, zirconium.
- IV. *The Alkaline Earths and Magnesium: The Ammonium Carbonate Group*  
Barium, calcium, magnesium, radium, strontium.
- V. *The Alkali Metals: The Soluble Group*  
Cesium, lithium, potassium, rubidium, sodium.

# OUTLINE OF A METHOD FOR THE DETECTION OF ALL METALLIC ELEMENTS

The following method of analysis<sup>2</sup> is based largely on the scheme devised by Noyes and Bray,<sup>3</sup> and has been adapted from the tables prepared by Treadwell and Hall.<sup>4</sup> The method is taken in its entirety from this source, but the form of the tables has been altered. It provides for the detection of all metals except certain rare earths, which are merely separated into groups.

One of the principal functions of these tables is to provide a method for the separation of the various metals from all interferences. In recent years numerous selective reagents have been described which permit the detection of traces of the elements with quantities of unknowns ranging down to one drop or less. A number of these are described in the section on Spot Tests (page 53). Many of these tests, however, are subject to interference, but when applied in conjunction with the following scheme, most qualitative problems are rather easily solved.

TABLE 3-1. PREPARATION OF THE SOLUTION

**1. Removal of Organic Matter.** If organic matter is present, oxidize it as follows: Take enough finely divided material to furnish about 1 g. of inorganic ash, cover it with 5 ml. of 9 *N* HClO<sub>4</sub> in a small casserole, and heat on the steam bath (not over a free flame). As soon as the liquid is hot, add cautiously, a drop at a time, 1 ml. of concentrated HNO<sub>3</sub>. Add more HNO<sub>3</sub> gradually (1-3 ml.) until no more nitrous fumes are evolved. Then heat the covered casserole on wire gauze over a small flame until fumes of HClO<sub>4</sub> are evolved. If a charred mass remains, cool, add 2 ml. more of HNO<sub>3</sub>, 3 ml. of HClO<sub>4</sub> and again evaporate, finally reducing the volume to 1-2 ml. If the organic matter is oil or fat, extraction with an organic solvent, such as ether, is better.

**2. Treatment with HBr and Br<sub>2</sub>.** Take 1 g. of finely divided material, or the liquid obtained in (1), and transfer to a 50-ml. round-bottomed flask. Insert a stopper carrying a thistle tube which reaches nearly to the bottom of the flask and a reflux tube 60 cm. long and of 0.8 cm. bore, extending to the bottom of the stopper. Connect the top of the reflux tube by delivery tubing with two right-angled bends leading to a test tube containing 5 ml. of saturated Br<sub>2</sub> water. Add slowly through the thistle tube 10 ml. of 9 *N* HBr and

<sup>2</sup> This section consists of a series of tables.

<sup>3</sup> Noyes, A. A., and Bray, W. C., *Qualitative Analysis of the Rare Elements*, Macmillan, New York, 1927.

<sup>4</sup> These tables are adapted from Treadwell, F. P., and Hall, W. T., *Analytical Chemistry*, Vol. I, 8th Ed., John Wiley and Sons, Inc., New York, 1932, with permission of the copyright owners.

TABLE 3-1. (Continued)

boil gently for 10 minutes. If the liquid in the test tube becomes colorless, add 10 drops of liquid  $\text{Br}_2$  from time to time. This treatment with  $\text{HBr}$  dissolves most substances. If a residue remains, cool to  $50^\circ$ , add 0.5 ml. of  $\text{Br}_2$  to the contents of the flask and heat 10 minutes on the steam bath, adding more  $\text{Br}_2$  if necessary. Cool to  $20^\circ$  and filter through an ashless paper if a residue remains. Treat the residue by (3) and the solution by (4). For the above treatment with  $\text{HBr}$  and  $\text{Br}_2$ , ground glass connections are desirable.

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**3. Decomposition of Silicates. Removal of  $\text{SiF}_4$  and  $\text{BF}_3$ .** Transfer the residue from (2), and the ash of the filter, to a small casserole and evaporate to dryness with 2 ml. of concentrated  $\text{HNO}_3$  to remove all halogen. Transfer to a platinum dish or crucible, evaporate to dryness, add 3–10 ml. of 27  $N$   $\text{HF}$  and heat over an air bath for 15 minutes. Then add 3 ml. of 9  $N$   $\text{HClO}_4$ , 2 ml. of concentrated  $\text{HNO}_3$  and heat to fumes of  $\text{HClO}_4$ . If an alkaline earth or rare earth fluoride dissolves slowly, heat 10 minutes longer with a little more  $\text{HClO}_4$ . Finally evaporate nearly to dryness and rinse into a small distilling flask with 2–3 ml. of water, as described under (4).

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**4. Distillation with  $\text{HBr}$ . Volatilization of  $\text{SeBr}_4$ ,  $\text{GeBr}_4$ , and  $\text{AsBr}_3$ .** Fuse some tubing to the side-arm of a small distilling flask and bend it so that the interior angle is about  $35^\circ$ . Transfer to this flask the solution obtained in (2) and the mixture obtained in (3). Distill carefully into the test tube and  $\text{Br}_2$  used in (2), keeping the latter chilled by ice around the tube. When the liquid in the flask has been reduced to 3 ml., it can be assumed that all  $\text{Se}$  and nearly all of the  $\text{Ge}$  and  $\text{As}$  have been expelled as bromides, the  $\text{AsBr}_3$  being converted to  $\text{H}_3\text{AsO}_4$  by the liquid in the receiver. Examine the distillate by Table 3-3 and the residue in the distilling flask by (5). Osmium and ruthenium do not volatilize as oxides by this treatment because the  $\text{HBr}$  serves to keep these elements at a valence lower than eight.

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**5. Distillation with  $\text{HNO}_3$  and  $\text{HClO}_4$ . Volatilization of  $\text{OsO}_4$  and  $\text{RuO}_4$ .** Cool the residual mixture in the distilling flask and add 4 ml. of 16  $N$   $\text{HNO}_3$  and 3 ml. of water. Distill off all  $\text{Br}_2$ , catching the distillate in a test tube containing 10 ml. of 6  $N$   $\text{NaOH}$  kept cold by immersion in ice water. After the  $\text{Br}_2$  is removed, carefully add  $\text{Na}_2\text{O}_2$  to the cold contents of the test tube until the liquid is colorless or about 1 g. of the powder has been used. Then continue distilling until only 4 ml. of liquid is left in the flask. A yellow or orange distillate shows that  $\text{Os}$  is probably present. In this case, add 2 ml. of water to the contents of the flask and again reduce to 4 ml. If the distillate is colored, add to it 2 ml. of alcohol and filter after 5 minutes. This serves to precipitate any  $\text{Ru}$  that may have distilled over. Filter and introduce  $\text{H}_2\text{S}$ . A black precipitate of  $\text{Os}_2\text{S}_3$  shows  $\text{Os}$  to be present. Now, to recover  $\text{RuO}_4$ , add 5 ml. of 9  $N$   $\text{HClO}_4$  and distill carefully till the volume is reduced to 3 ml., catching the distillate in 12 ml. of 6  $N$   $\text{NaOH}$  which changes  $\text{RuO}_4$  to  $\text{Na}_2\text{RuO}_5$ . This yields an orange to dark red solution. If a red precipitate of  $\text{HgO}$  is formed, as sometimes happens when much  $\text{Hg}$  is present, filter it off, using an asbestos filter. If the distillate is colored, add 2 ml. more of 9  $N$   $\text{HClO}_4$  to the flask and distill again to a volume of 3 ml. To the distillate add 2 ml. of alcohol: a black precipitate is  $\text{Ru}$ . Treat the residue in the flask by (6).

If  $\text{Os}$  and  $\text{Ru}$  are not likely to be present, this procedure can be shortened by merely adding 4 ml. of 16  $N$   $\text{HNO}_3$  to the residual mixture from (4), evaporating off half the solution, adding 5 ml. of 9  $N$   $\text{HClO}_4$  and distilling to 3 ml. In this way the  $\text{HBr}$  is replaced by  $\text{HClO}_4$ , which is advantageous for the next treatment.

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TABLE 3-1. (Continued)

**6. Precipitation of W, Ta, and Au groups. Partial removal of alkalis.** To the cold residue in the distilling flask, add slowly 10 ml. of 12 *N* formic acid and boil under a reflux condenser for 15 minutes. Filter while hot through a hardened, ashless filter and wash with a little hot water. Treat the residue by (7). Evaporate the filtrate to about 10 ml. and cool. Examine any precipitate for K, Rb, and Cs as described in Table 3-12, and the solution by Table 3-7.

**7. Extraction of the W and Ta groups.** Treat the first residue obtained in (6) in a platinum or plastic dish with about 10 ml. of 27 *N* HF and heat 10 minutes on the steam bath. Filter through a hardened filter in a plastic funnel and catch the filtrate in a platinum dish. Wash thoroughly. Treat the residue by (8) and examine the filtrate for the W and Ta groups by Table 3-4.

**8. Treatment with hot sodium carbonate solution.** All insoluble fluorides except  $\text{ThF}_4$  and some  $\text{CaF}_2$ , together with any  $\text{BaSO}_4$ , are converted quite completely to carbonates by this treatment which consists in boiling the residue from (7) with 50 ml. of 3 *N*  $\text{Na}_2\text{CO}_3$  to which 10 g. of solid  $\text{Na}_2\text{CO}_3$  are added as soon as the solution is boiling. Boil 15 minutes under a reflux condenser. Filter and reject the filtrate. To the well-washed residue, add 10 ml. of 3 *N*  $\text{HClO}_4$ , treat the resulting solution by Table 3-8, testing especially for Pb, Ca, Sr, and Bi. Treat the residue by (9).

**9. Extraction of the Au group and Ag.** Cover the residue from (8) with 9 ml. of 16 *N*  $\text{HNO}_3$  and 3 ml. of 2 *N*  $\text{HCl}$  and heat 10 minutes on the steam bath. Evaporate nearly to dryness, add 12 ml. of water, boil, and filter. Analyze the filtrate by Table 3-6. Digest the residue with 10 ml. of warm, 15 *N*  $\text{NH}_4\text{OH}$  and filter. Boil off most of the  $\text{NH}_3$  and test for Ag with  $\text{HCl}$ . Examine the last residue by Table 3-2.

TABLE 3-2. TREATMENT OF MATERIAL UNATTACKED BY TREATMENT OF TABLE 3-1

**1. Residue from Table 3-1, 9.** If the residue is nonmetallic, it is likely to contain oxides of Al, Cr, Ti, and Sn; phosphates of Ti, Zr, Th, Ce, and other rare earths, an undecomposable silicate, sulfates of Ba and Cr, fluorides of Th and Ca, metallic Ir and Rh, C. Fuse a nonmetallic residue with 10 g. of  $\text{K}_2\text{S}_2\text{O}_7$  in a silica crucible for 20 minutes. Loosen the melt and reduce it to powder with mortar and pestle. Digest with 25 ml. of cold water for some time, filter, heat the residue with 10 ml. of 12 *N*  $\text{HCl}$ , evaporate to 1 ml., add 5 ml. of water, filter and unite the filtrate with that just obtained. Examine the residue by (2) and the united filtrates by (8). If the residue from Table 3-1 is metallic, fuse with  $\text{Na}_2\text{O}_2$  as described below under (6).

**2.** The residue may contain Pb, Ba, Sr, Ca, and Cr as sulfates; Si, W, Ta, and Nb as oxides, metallic Ir, unattacked silicate or  $\text{SnO}_2$ . Treat with HF by Table 3-1, 7. Examine the residue by (3) and the solution by (4).

**3. Residue from 2.** The residue may contain Ba and Cr as sulfates; Pb, Sr, and Ca as fluorides, unattacked silicate, metallic Ir or  $\text{SnO}_2$ . Boil with  $\text{Na}_2\text{CO}_3$  as in Table 3-1, 8. Filter and reject the filtrate.

TABLE 3-2. (Continued)

4. **Solution from 2.** Test for W, Ta and Nb as described in Tables 3-4 and 3-5.

5. **Residue from 3.** The residue may contain Pb, Ba, Sr, and Ca as carbonates, Cr as hydroxide, a silicate, metallic Ir or  $\text{SnO}_2$ . Treat with  $\text{HClO}_4$  as in Table 3-1, 8.

6. **Residue from 5.**  $\text{Cr}_2(\text{SO}_4)_3$ , silicate,  $\text{SnO}_2$ , Ir. Metallic residue from Table 3-1 of Pt metals and alloys. Fuse with 5 g. of  $\text{Na}_2\text{O}_2$  in a nickel crucible, gradually raising the temperature and heating the bottom of the crucible 15 minutes at dull redness. Cool, extract with 30 ml. of cold water, remove the crucible and decompose excess  $\text{Na}_2\text{O}_2$  by boiling. Neutralize with 12 *N* HCl added in small portions while cooling. Add 1 ml. of alcohol and 2.5 ml. more of HCl. Heat on the steam bath. If a residue remains, filter, digest it 10 minutes with 5 ml. of 12 *N* HCl and 1 ml. of 15 *N*  $\text{HNO}_3$ , evaporate to small volume, add water and unite with the main solution without filtering. Cool, saturate with  $\text{H}_2\text{S}$  in a 100-ml. pyrex bottle, stopper and heat in water for an hour. Cool, open the bottle, add more  $\text{H}_2\text{S}$  if necessary and heat again. Filter and analyze the filtrate for the Al, Ni, and rare earth groups, remembering that Ni comes from the crucible. Transfer the  $\text{H}_2\text{S}$  precipitate to a flask and treat by Table 3-1, 2, without filtering, and then by Table 3-1, 4. Analyze the distillates by Table 3-3, and for Os and Ru. Treat the residual liquid by Table 3-1, 6, and the filtrate obtained here for Ag and the Cu-Te groups. Follow by Table 3-1, 7 and 9 etc., repeating the  $\text{Na}_2\text{O}_2$  fusion. If there is a residue, dry it, treat by (8) and combine any  $\text{H}_2\text{S}$  precipitate with the main precipitate. Reject the filtrate.

7. **Solution from 5.** Test for Pb, Ba, Sr, and Ca in the usual way. See Table 3-11.

8. **Filtrate from 1.** Adjust the acidity as described in Table 3-8, 1. Saturate with  $\text{H}_2\text{S}$  and filter.

9. **Precipitate from 8.** Sulfides of Se, As, Sb, and Sn; Te and Cu groups. Treat with HBr as in Table 3-1, 2 and 4 and test the distillate for Se and As by Table 3-3.

10. **Residue from 9.** Evaporate with  $\text{HNO}_3$  and  $\text{HClO}_4$ , boil with 12 *N*  $\text{HCO}_2\text{H}$  as in Table 3-1, 5 and 6.

11. **Residue from 10.** Oxides of Sn and Sb. Treat with 10 ml. of 12 *N* HCl, dilute with water to 55 ml., heat, and saturate with  $\text{H}_2\text{S}$ . Filter.

12. **Precipitate from 11.**  $\text{Sb}_2\text{S}_3$ . Dissolve in 5 ml. concentrated HCl. If not clear, add 5 ml. water and filter. Reject residue. Evaporate filtrate to 2 ml., cool and add metallic tin. Let stand 10 minutes. A black residue, insoluble in  $\text{NaBrO}$ , is antimony.

13. **Filtrate from 11.** Add 4 ml. concentrated  $\text{NH}_4\text{OH}$  and saturate with  $\text{H}_2\text{S}$ . Let stand 10 minutes. If no precipitate forms, tin is absent. If a precipitate forms, evaporate (without filtering) to 15 ml. Add powdered Sb and boil gently 2 minutes. Filter, and add 2 ml. HCl and a little  $\text{HgCl}_2$  solution. A white or gray precipitate indicates Sn.

14. **Filtrate from 9.** Treat with  $\text{H}_2\text{S}$  and examine the precipitate for the Te and Cu groups by Table 3-8.



TABLE 3-2. (Continued)

**15. Filtrate from 8.** Analyze for Tl and according to Tables 3-7 and 3-10. In Table 3-10, 3, test the  $\text{FeCl}_2$  for Tl, after removing  $\text{GaCl}_3$ , by adding 2-3 ml. of  $N$  KI solution. A yellow precipitate is TlI.

TABLE 3-3. ANALYSIS OF THE SELENIUM GROUP

Distillate from Table 3-1, 4, containing  $\text{SeBr}_4$ ,  $\text{H}_3\text{AsO}_4$ , and  $\text{GeBr}_4$  in solution with  $\text{HBr}$  and  $\text{Br}_2$ .

**1. Precipitation of Se.** To the solution add  $\text{Na}_2\text{S}_2\text{O}_5$  dropwise, keeping the liquid cold, until the excess  $\text{Br}_2$  is almost but not quite removed. An excess of sulfite must be avoided as it yields S with  $\text{H}_2\text{S}$ . Add 1 ml. of 3  $M$   $\text{NH}_2\text{OH} \cdot \text{HCl}$  solution and heat 5 minutes without boiling. If much precipitate forms, add more hydroxylamine salt. Cool and filter.

**2. Precipitate from 1.** A red precipitate which darkens on heating is Se. The precipitate often forms very slowly.

**3. Filtrate from 1.** Saturate the filtrate from (1) with  $\text{H}_2\text{S}$  using a stout bottle, and heat the stoppered bottle in boiling water. Cool, add more  $\text{H}_2\text{S}$  and filter after 10 minutes. Wash the precipitate with a little 6  $N$   $\text{H}_2\text{SO}_4$  saturated with  $\text{H}_2\text{S}$ . Reject the filtrate.

**4. Precipitate from 3.** Treat the precipitate of  $\text{As}_2\text{S}_5$ ,  $\text{As}_2\text{S}_3$ , S and  $\text{GeS}_2$  with about 10 ml. 6  $N$   $\text{NH}_4\text{OH}$  thereby forming  $(\text{NH}_4)_3\text{AsO}_4$ ,  $(\text{NH}_4)_3\text{AsS}_4$ ,  $(\text{NH}_4)_2\text{GeO}_3$ ,  $(\text{NH}_4)_2\text{GeS}_3$ , etc. To the solution in a platinum or plastic dish add two-thirds as much 27  $N$  HF as there was used of  $\text{NH}_4\text{OH}$ . Cool and saturate with  $\text{H}_2\text{S}$ . Filter into a platinum dish.

**5. Precipitate from 4.**  $\text{As}_2\text{S}_5$ ,  $\text{As}_2\text{S}_3$ . To the As precipitate add 4 ml. of 6  $M$   $\text{NH}_4\text{OH}$  and 3 ml.  $\text{H}_2\text{O}_2$ . Heat to boiling and filter. Discard any residue. To the filtrate add 3 ml. of magnesia mixture, cool and stir vigorously. A white precipitate of  $\text{MgNH}_4\text{AsO}_4$  indicates As. This is confirmed as follows: Filter, wash, and to the precipitate add  $\text{AgNO}_3$  solution and HAc. A red precipitate of  $\text{Ag}_3\text{AsO}_4$  forms if As is present.

**6. Filtrate from 4.** To the filtrate containing  $\text{H}_2\text{GeF}_6$ , add 5 ml. of concentrated  $\text{H}_2\text{SO}_4$ , evaporate to fumes, cool, and pour into 25 ml. of water. Saturate with  $\text{H}_2\text{S}$  and filter. Reject the filtrate.

**7. Precipitate from 6.** White  $\text{GeS}_2$ . Dissolve the well-washed precipitate in 3  $N$   $\text{NH}_4\text{OH}$  and evaporate the solution to dryness in platinum. Add 1-3 ml. of HF solution and heat to boiling. Filter if not clear. Evaporate the solution of  $\text{H}_2\text{GeF}_6$  to dryness, add 10 drops of HF and the same quantity of 6  $N$   $\text{K}_2\text{CO}_3$  solution and 1 ml. of water. Heat to boiling and let stand 15 minutes. A greyish-white precipitate of  $\text{K}_2\text{GeF}_6$  shows Ge to be present.

TABLE 3-4. SEPARATION OF TANTALUM AND TUNGSTEN GROUPS  
ANALYSIS OF THE TUNGSTEN GROUP

**1. Separation of W and Ta groups.** To the HF solution of Table 3-1, 7, add 2 ml. of concentrated  $\text{H}_2\text{SO}_4$  and evaporate to dense fumes. Cool, carefully add 5 ml. of water, and transfer to a pressure bottle. Make ammoniacal, add 10 ml. of fresh, 6  $N$   $(\text{NH}_4)_2\text{S}$  solution, stopper the bottle, place in a dish of water, and heat the water to boiling. Add more  $(\text{NH}_4)_2\text{S}$  if necessary and heat for 30 minutes with occasional shaking. Cool, filter, and wash with hot water. If the residue is orange or brown in color, or is very large, heat it with 3  $N$   $\text{NH}_4\text{OH}$ , filter, and add the filtrate to that just obtained.

**2. Residue from 1.**  $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ , Ti and Zr phosphates or vanadates,  $\text{Bi}_2\text{S}_3$ . Examine by Table 3-5.

**3. Filtrate from 1.** Pour the ammoniacal solution of thio salts very slowly, while stirring, into 40 ml. of 6  $N$   $\text{H}_2\text{SO}_4$ . Filter through asbestos in a Gooch crucible, wash with hot water, and dry at  $100\text{--}125^\circ$ .

**4. Precipitate from 3.** Place the dried sulfides of Sb, Sn, W, Mo, Te, and V in a combustion tube and heat in a stream of  $\text{H}_2\text{S}$  at  $500\text{--}600^\circ$  for 30 minutes. Cool in an atmosphere of  $\text{H}_2\text{S}$ . Treat the residue and sublimate with 10 ml. of 12  $N$   $\text{HCl}$  as described in Table 3-2, 11, testing the resulting solution for Sb and Sn as there described. Examine the residue by (6).

**5. Filtrate from 3.** When  $\text{H}_3\text{PO}_4$  is present, sometimes nearly all of the W is found in the filtrate from 3, but in the absence of  $\text{H}_3\text{PO}_4$  it is precipitated for the most part as  $\text{WS}_3$ . Test one-tenth of the solution for phosphate with  $(\text{NH}_4)_2\text{MoO}_4$ , and if a yellow precipitate is obtained, evaporate the remainder of the solution to dense fumes, add cautiously 1 ml. of 16  $N$   $\text{HNO}_3$ , and fume again. Add 1 ml. of 12  $N$   $\text{HCl}$  and evaporate just to dryness. Add 3 ml. of  $\text{SnCl}_2$  and heat. Add 3 ml. of 12  $N$   $\text{HCl}$  and heat again. An intense blue color shows W to be present.

**6. Residue from 4.**  $\text{WS}_2$ ,  $\text{MoS}_2$ , Te,  $\text{V}_2\text{S}_3$ , asbestos. Dissolve in a mixture of equal parts 12  $N$   $\text{HCl}$  and 16  $N$   $\text{HNO}_3$ , evaporate nearly to dryness, add 5 ml. of 6  $N$   $\text{NH}_4\text{OH}$ , heat and filter off the asbestos. Evaporate just to dryness, add 10 ml. of 12  $N$   $\text{HCl}$ , heat 10 minutes on the water bath, evaporate to dryness again, take up in 40 ml. of 2  $N$   $\text{HCl}$ , boil gently and filter. Examine the residue by (7) and the filtrate by (8).

**7. Residue from 6.**  $\text{H}_2\text{WO}_4$ . Dissolve in a little 15  $N$   $\text{NH}_4\text{OH}$ . Evaporate almost to dryness, add 3 ml. of  $N$   $\text{SnCl}_2$ , heat to boiling. Add 3 ml. of 12  $N$   $\text{HCl}$ , heat to boiling again and allow to cool. A blue precipitate of  $\text{W}_2\text{O}_5 \cdot x\text{WO}_3$  shows W to be present.

**8. Filtrate from 6.**  $\text{H}_2\text{MoO}_4$ ,  $\text{H}_2\text{TeO}_3$ ,  $\text{VOCl}_2$ . Dilute the solution with three times as much water, saturate with  $\text{H}_2\text{S}$ , and heat in a pressure bottle as in (1). Cool, open the bottle, and filter.

**9. Precipitate from 8.**  $\text{MoS}_3$ , Te. Dissolve by heating with 6 ml. of 12  $N$   $\text{HCl}$  and 2 ml. of 16  $N$   $\text{HNO}_3$ . Evaporate to dryness, add 1 ml. of 6  $N$   $\text{HCl}$  and 5 ml. of water. Test with 5 ml. of  $\text{KCNS}$  and 0.1 g. of metallic Zn. A red solution of  $\text{MoO}(\text{CNS})$  shows Mo to be present. A black precipitate is Te.

TABLE 3-4. (Continued)

10. Filtrate from 8.  $\text{VOCl}_3$ . Evaporate to dryness, add 2 ml. of 16  $N$   $\text{HNO}_3$  and again evaporate. Add 5 ml. of 6  $N$   $\text{NH}_4\text{OH}$  and saturate with  $\text{H}_2\text{S}$ . A violet-red color shows  $\text{V}$  to be present. As a confirmatory test, evaporate to dryness, add a little  $\text{HNO}_3$ , 3 ml. of water, and 1 ml. of  $\text{H}_2\text{O}_2$ . A reddish-brown color of  $\text{HVO}_4$  indicates vanadium.

TABLE 3-5. ANALYSIS OF THE TANTALUM GROUP

1. Residue of Table 3-4, 2:  $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Ti}(\text{HPO}_4)_2$ ,  $\text{Zr}(\text{HPO}_4)_2$ ,  $\text{Ti}(\text{HVO}_4)_2$ ,  $\text{Zr}(\text{HVO}_4)_2$ ,  $\text{Bi}_2\text{S}_3$ . Boil for 2 hours in a liter flask with 350-400 ml. of an aqueous solution of 5 g.  $\text{Na}_2\text{CO}_3$  and 15 g. salicylic acid. Filter through an ashless paper.

2. Residue from 1.  $\text{Ta}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{ZrO}_2$ ,  $\text{Zr}(\text{HPO}_4)_2$ ,  $\text{Bi}_2\text{S}_3$ . Treat in a platinum crucible with a little  $\text{HF}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$  to remove any  $\text{SiO}_2$ . Evaporate to dryness and fuse with 5 g.  $\text{K}_2\text{CO}_3$  and 0.1 g.  $\text{KNO}_3$ . Leach the melt with 10 ml. of cold water, stirring well. Filter and wash with cold water.

3. Residue from 2.  $\text{ZrO}_2$ ,  $\text{Bi}_2\text{O}_3$ . Fuse with 3 g.  $\text{K}_2\text{S}_2\text{O}_7$ . Cool, extract with 20 ml. of water, heating till all soluble salt has dissolved. Without filtering add  $\text{H}_2\text{S}$ , and then filter.

4. Precipitate from 3: A black precipitate is probably  $\text{Bi}_2\text{S}_3$ . Dissolve the precipitate in 3  $N$   $\text{HNO}_3$ , filter, and precipitate  $\text{Bi}(\text{OH})_3$  with an excess of  $\text{NH}_4\text{OH}$ . Filter, wash, and add to the precipitate a little freshly prepared  $\text{NaHSnO}_2$  solution. An immediate blackening indicates  $\text{Bi}$ .

5. Filtrate from 3.  $\text{ZrOSO}_4$ . Expel  $\text{H}_2\text{S}$ , add 2 ml. of 2  $N$   $\text{H}_2\text{O}_2$  and 10 ml. of  $N$   $\text{Na}_2\text{HPO}_4$ . A white precipitate is  $\text{Zr}(\text{HPO}_4)_2$ .

6. Filtrate from 2.  $\text{K}_5\text{Ta}_6\text{O}_{19}$ ,  $\text{K}_8\text{Nb}_6\text{O}_{19}$  and  $\text{K}_2\text{HPO}_4$ . Dilute to 25 ml., saturate with  $\text{SO}_2$  and heat 30 minutes while passing this gas through the solution. Filter through a plastic funnel.

7. Precipitate from 6. White  $\text{Ta}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ . Dissolve from the filter with a little  $\text{HF}$ , catching the filtrate in a platinum crucible. Add a little concentrated  $\text{HNO}_3$ , evaporate to dryness, add 2 ml. of  $\text{HF}$  and 0.5 g. of  $\text{K}_2\text{CO}_3$ . Evaporate to dryness and heat gently until the residue becomes enamel-white, but not allowing even the bottom of the crucible to become dull-red. Dissolve in a little water, evaporate to 0.5 ml., add 4 ml. of water, heat to boiling and filter after 15 minutes.

8. Precipitate from 7. Greyish-white, viscous appearing  $2\text{K}_2\text{TaF}_7 \cdot \text{Ta}_2\text{O}_5$ . Treat again by the above procedure in (7) if the appearance of the precipitate is not satisfactory.

9. Filtrate from 7.  $\text{K}_2\text{NbF}_6$ . Fume with  $\text{H}_2\text{SO}_4$ , add  $\text{NH}_4\text{OH}$ , boil, make acid with  $\text{H}_2\text{SO}_4$ , and boil again. A white precipitate is  $\text{Nb}_2\text{O}_5$ . Filter, using a plastic funnel. Dissolve the precipitate in 2 ml. of  $\text{HF}$ , add 1 ml. of  $\text{H}_2\text{SO}_4$ , and evaporate to fumes. Cool, add dropwise 1 ml. of 6  $N$   $\text{HCl}$ , keeping the mixture cool. Add about 25 mg. of powdered zinc: a blue color indicates the presence of  $\text{NbCl}_3$ . Pour the solution through

TABLE 3-5. (Continued)

a zinc reductor that has been washed with 0.3 *N* HCl into a mixture of 5 ml. 0.2 *N* HgCl<sub>2</sub> and 0.5 ml. of 6 *N* HCl. A white precipitate of Hg<sub>2</sub>Cl<sub>2</sub> confirms the presence of Nb.

**10. Filtrate from 1. Ti salicylate, H<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>VO<sub>4</sub>.** Evaporate to 50 ml. Cool, transfer to a 200-ml. separatory funnel and add gradually 6 ml. of 18 *N* H<sub>2</sub>SO<sub>4</sub>. Cool and shake with 40 ml. of ether. Treat the aqueous layer with two other 10-ml. portions of ether, finally discarding all the ether-salicylic acid solutions. Evaporate the aqueous layer to 20 ml., add an excess of NaOH, boil, and filter.

**11. Precipitate from 10. TiO<sub>2</sub>.** Dissolve in a little, hot, 6 *N* HNO<sub>3</sub> containing a little H<sub>2</sub>O<sub>2</sub>. If the orange color of TiO<sub>2</sub>·H<sub>2</sub>O<sub>2</sub> develops, add 3 ml. of 6 *N* H<sub>2</sub>SO<sub>4</sub>, evaporate to fumes, add water, some more H<sub>2</sub>O<sub>2</sub> and some Na<sub>2</sub>HPO<sub>4</sub>. If a precipitate of Zr(HPO<sub>4</sub>)<sub>2</sub> forms after standing at least an hour, filter if off. To the filtrate, add powdered Na<sub>2</sub>SO<sub>3</sub>. A white precipitate of Ti(HPO<sub>4</sub>)<sub>2</sub> forms if Ti is present.

**12. Filtrate from 10. Na<sub>3</sub>VO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub>.** Test for phosphoric acid in one-fifth of the filtrate with HNO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>. Treat the remainder of the solution as in Table 3-4, 10, to see if V is present here.

TABLE 3-6. ANALYSIS OF THE GOLD GROUP

**1. Solution from Table 3-1, 9: Chlorides of Hg, Au, Pt, Pd, possibly Ir and Rh.** If the solution is colorless, there is not much of these elements present except Hg. To a colorless solution, therefore, merely add a few drops of *N* SnCl<sub>2</sub>. A gray precipitate indicates mercury. To a colored solution, add 1 drop of 6 *N* HCl and shake vigorously for 1 minute with 10 ml. of pure ethyl acetate in a short-stemmed separatory funnel. Draw off the aqueous layer and shake it again with a fresh portion of ethyl acetate.

**2. Ethyl acetate solution from 1: HgCl<sub>2</sub>, AuCl<sub>3</sub>.** Shake the second ethyl acetate solution vigorously for 1 minute with 8 ml. of 3 *N* NH<sub>4</sub>Cl. Draw off the lower aqueous layer and shake this with the first ethyl acetate solution. Unite the two remaining ethyl acetate solutions.

**3. Ethyl acetate solution from 2:** If the solution is yellow, AuCl<sub>3</sub> is indicated. Evaporate to dryness in a small casserole and ignite to dull redness. Add 1 ml. of 12 *N* HCl and a few drops of 16 *N* HNO<sub>3</sub>. Add a little water and some KI, and boil. If there is considerable precipitate, add more iodide. A red or purple precipitate is Au.

**4. Aqueous solution from 2: (NH<sub>4</sub>)<sub>2</sub>HgCl<sub>4</sub>.** Add an equal volume of 6 *N* NH<sub>4</sub>OH and a little KI. Heat and let stand 5 minutes. An orange or yellow precipitate is HgO·HgINH<sub>2</sub>.

**5. Aqueous solution from 1: H<sub>2</sub>PtCl<sub>6</sub>, H<sub>2</sub>IrCl<sub>6</sub>, H<sub>2</sub>PdCl<sub>4</sub>, H<sub>3</sub>RhCl<sub>6</sub>.** Add 5 ml. of 12 *N* HCl and evaporate nearly to dryness. Add a little water and evaporate until there is no odor of HCl. If the residue is colorless no Pt, Ir, Pd, or Rh is present. To a colored residue, add 2 drops of 6 *N* HCl, transfer with 1 ml. of water to a weighing bottle, add an excess of NH<sub>4</sub>Cl powder, and allow to stand half an hour in ice water. Filter and wash with cold NH<sub>4</sub>Cl solution.

TABLE 3-6. (Continued)

**6. Precipitate from 5.**Yellow crystals:  $(\text{NH}_4)_2\text{PtCl}_6$ Black precipitate:  $(\text{NH}_4)_2\text{IrCl}_6$ 

Red precipitate: both of these

Dissolve by heating with 15 ml. of 12 *N* HCl and 1.0 ml. of 16 *N* HNO<sub>3</sub>. Evaporate on the steam bath until all excess acid is removed, add NaHCO<sub>3</sub> solution until basic to litmus, cool, add a little more NaHCO<sub>3</sub> solution, a little Br<sub>2</sub> water, and heat 10 minutes on the steam bath.

**7. Black precipitate from 6. IrO<sub>2</sub>. Test the precipitate for Ir by Table 3-8, 9.**

**8. Filtrate from 6. Na<sub>2</sub>PtCl<sub>6</sub>.** Make acid with HCl, evaporate to dryness, and treat with NH<sub>4</sub>Cl as in (5). A yellow or orange precipitate is  $(\text{NH}_4)_2\text{PtCl}_6$ .

**9. Filtrate from 5:  $(\text{NH}_4)_2\text{PdCl}_6$ ,  $(\text{NH}_4)_3\text{RhCl}_6$ .** Saturate with Cl<sub>2</sub> gas in a bottle, stopper it, and allow to stand 30 minutes. Filter.

**10. Red precipitate from 9.  $(\text{NH}_4)_2\text{PdCl}_6$ .**

**11. Red filtrate from 9:  $(\text{NH}_4)_3\text{RhCl}_6$ .** Test for Rh as in Table 3-8, 11.

TABLE 3-7. ANALYSIS OF THE THALLIUM GROUP

**1. Filtrate from Table 3-1, 6:** Perchlorates of elements other than Se, As, Ge, Os, Ru, Sb, Sn, W (may be present as phosphotungstic acid) Nb, Ta, Au, Hg, Pt, and Pd. A few mg. of Mo (more if P is present) and Ti (more if Zr is present) may be found here, although these elements normally are found in the preceding groups. To the solution, add an excess of HBr, shake and filter after 5 minutes, washing with cold, *N* HBr. (The HBr used should not contain free Br<sub>2</sub>, which will oxidize Tl. To 9 *N* HBr add an equal volume of 12 *N* HCO<sub>2</sub>H, 2 5 volumes of water, and boil a few minutes.)

**2. Precipitate from 1: AgBr, TlBr, PbBr<sub>2</sub>.** Treat with hot water until all PbBr<sub>2</sub> and TlBr have dissolved, as shown by testing the filtrate with K<sub>2</sub>CrO<sub>4</sub>. Then treat with 15 ml. of saturated Br<sub>2</sub> water, which oxidizes TlBr to soluble TlBr<sub>3</sub>. Filter.

**3. Residue from 2: AgBr.** Warm with 10 ml. of 15 *N* NH<sub>4</sub>OH with occasional stirring. Although AgBr is much less soluble than AgCl, this treatment serves to form sufficient  $[\text{Ag}(\text{NH}_3)_2]^+$  to give a test for Ag when the solution is acidified with HNO<sub>3</sub>. A yellowish precipitate indicates silver.

**4. Solution from 2: PbBr<sub>2</sub>, TlBr<sub>3</sub>.** Add H<sub>2</sub>SO<sub>4</sub>, filter, and wash with a very little 2 *N* H<sub>2</sub>SO<sub>4</sub>.

**5. Precipitate from 4: PbSO<sub>4</sub>.** Dissolve the precipitate in 10 ml. of 3 *N* NH<sub>4</sub>Ac, and to the solution add a few drops K<sub>2</sub>CrO<sub>4</sub> solution and 3 ml. 6 *N* HAc. A yellow precipitate of PbCrO<sub>4</sub> indicates Pb.

TABLE 3-7. (Continued)

6. **Filtrate from 4:**  $\text{Ti}_2(\text{SO}_4)_3$ . Add powdered  $\text{Na}_2\text{SO}_3$  in slight excess to reduce the  $\text{Ti}^{+++}$  to  $\text{Ti}^+$  and add 2 ml. of  $N$  KI. A yellow precipitate is  $\text{TiI}$ .

7. **Filtrate from 1:** Analyze by Table 3-8.

TABLE 3-8. ANALYSIS OF TELLURIUM AND COPPER GROUPS

1. **Filtrate from Table 3-7, 1:** Evaporate the  $\text{HClO}_4$  solution from Table 3-7 until bubbles of gas escape on removing the flame, but do not evaporate to strong fumes. Measure the volume and assume 9 milliequivalents of acid are present in each ml. Add 25 ml. of water and  $\text{HCl}$  (or  $\text{NH}_4\text{OH}$ ) to make exactly 30 milliequivalents of acid present in all. Add 4 ml. of 3  $N$   $\text{NH}_4\text{Cl}$ , heat in a vessel immersed in boiling water, and saturate with  $\text{H}_2\text{S}$ . Dilute with water to 100 ml., saturate again with  $\text{H}_2\text{S}$ , and let stand 15 minutes. Filter and wash with hot water.

If Ir is to be tested for, or if some Mo is unprecipitated, evaporate the filtrate to 5 ml., add 10 ml. of 6  $N$   $\text{HCl}$ , boil with reflux condensation for 10 minutes to convert the perchlorate of Ir to chloride. Cool, transfer to a 100-ml. pyrex bottle, saturate with  $\text{H}_2\text{S}$ , stopper, and heat in gently boiling water for half an hour. Cool, filter, and wash with hot water. Unite the precipitate with that obtained before. Examine the filtrate by Table 3-10 after adding 10 ml. 6  $N$   $\text{NH}_4\text{OH}$ .

2. **Precipitate from 1: Sulfides of Te, Mo, Ir, Rh, Pb, Bi, Cu, and Cd.** Dissolve in 10 ml. of 12  $N$   $\text{HCl}$  and 2 ml. of 16  $N$   $\text{HNO}_3$ . Evaporate to dryness. Add 6 ml. of 12  $N$   $\text{HCl}$  and saturate the cold solution with  $\text{SO}_2$ . Filter and reject any precipitate of Se that may form. The Te is not precipitated in the strong acid solution. Add 20 ml. of water, saturate again with  $\text{SO}_2$ , and heat 15 minutes in boiling water. Filter, and wash with hot water.

3. **Precipitate from 2: Black Te.**

4. **Filtrate from 2:** Evaporate nearly to dryness. Add a few drops of 16  $N$   $\text{HNO}_3$  and evaporate to dryness on the steam bath. Add 5 ml. of 6  $N$   $\text{HCl}$  and shake the cold, acid solution with two, 15-ml. portions of ether in a separatory funnel. Unite the ether extracts and wash them with two 2-ml. portions of 6  $N$   $\text{HCl}$ .

5. **Ether solution from 4:  $\text{MoO}_3$ ,  $2\text{HCl}$ .** Evaporate to dryness on the steam bath and dry over a small moving flame. A dark blue residue is  $\text{Mo}_2\text{O}_5 \cdot x\text{MoO}_3$ . Add  $\text{HCl}$  and a little  $\text{HNO}_3$  and again evaporate. Dissolve in 2 ml. of 6  $N$   $\text{HCl}$ , add 5 ml. of water and 5 ml. of  $N$   $\text{KCNS}$ . Add a little zinc. Decant off the solution and add  $\text{H}_2\text{S}$ . A brown precipitate is  $\text{MoS}_3$ .

6. **Aqueous solution from 4:** Evaporate just to dryness, add 1 ml. of 6  $N$   $\text{HAc}$ , 10 ml. of water, and 5 ml. of 3  $N$   $\text{NaNO}_2$ . Heat 5 minutes at 60–70°. Cool, add 6  $N$   $\text{NaOH}$  in 0.5-ml. portions until the solution is basic. Dilute with 20 ml. of water if a large precipitate forms. Filter and wash with hot water. To the filtrate, add 5 ml. of  $N$   $\text{NaHCO}_3$  solution and, if there is any precipitate, filter through a new filter but unite this precipitate with that previously obtained.

TABLE 3-8. (Continued)

7. **Precipitate from 6: Hydroxides of Pb, Bi, Cu, and Cd.** Dissolve in  $\text{HNO}_3$  and analyze for these elements as in Table 3-9.

8. **Filtrate from 6:  $\text{Na}_3\text{Ir}(\text{NO}_2)_6$ ,  $\text{Na}_3\text{Rh}(\text{NO}_2)_6$ .** Add 5 ml. of 12  $N$   $\text{HCl}$  and evaporate just to dryness. Dissolve in 15 ml. of water, and add 2 ml. of 3  $N$   $\text{Na}_2\text{CO}_3$  solution. Heat in a water bath, cool, add 2 ml. more of  $\text{Na}_2\text{CO}_3$  solution and 2 drops of liquid  $\text{Br}_2$ , shaking till it dissolves. Heat 10 minutes in boiling water. Filter and wash with hot water. Reject the filtrate.

9. **Precipitate from 8: Blue-black  $\text{IrO}_2$  and green  $\text{RhO}_2$ .** Heat the precipitate in a small casserole with a little 9  $N$   $\text{HBr}$ , until it dissolves. To the residue add 2 drops of 6  $N$   $\text{HCl}$ , transfer to a weighing bottle, saturate with  $\text{Cl}_2$ , stopper, and heat at  $50^\circ$  for 5 minutes. Cool, add powdered  $\text{NH}_4\text{Cl}$  as in Table 3-6, 5.

10. **Precipitate from 9: Black  $(\text{NH}_4)_2\text{IrCl}_6$ .**

11. **Red solution from 9:  $(\text{NH}_4)_3\text{RhCl}_6$ .** Add 3 ml. of 15  $N$   $\text{NH}_4\text{OH}$  and evaporate just to dryness. To the residue add 3 ml. of 6  $N$   $\text{HCl}$ , boil, transfer to a weighing bottle, and let stand 30 minutes. A light yellow precipitate is  $\text{RhCl}(\text{NH}_3)_5\text{Cl}_2$ .

TABLE 3-9. ANALYSIS OF COPPER GROUP

1. **Precipitate from Table 3-8, 7: Hydroxides of Pb, Bi, Cu, and Cd.** Dissolve in 2  $N$   $\text{HNO}_3$ , add 6  $N$   $\text{H}_2\text{SO}_4$  to precipitate lead, and evaporate to fumes of  $\text{SO}_3$ . Cool, pour into water, and filter.

2. **Precipitate from 1:  $\text{PbSO}_4$ .** Dissolve in 10 ml. of 3  $N$   $\text{NH}_4\text{Ac}$ , and to the solution add a few drops of  $\text{K}_2\text{CrO}_4$  solution and 3 ml. 6  $N$   $\text{HAc}$ . A yellow precipitate of  $\text{PbCrO}_4$  indicates Pb.

3. **Filtrate from 1: Bi, Cu, Cd.** Add an excess of  $\text{NH}_4\text{OH}$ , filter, and wash.

4. **Precipitate from 3:  $\text{Bi}(\text{OH})_3$ .** Treat the precipitate with a little freshly prepared  $\text{NaHSnO}_2$  solution. An immediate blackening indicates Bi.

5. **Filtrate from 3:  $[\text{Cu}(\text{NH}_3)_4]^{++}$  and  $[\text{Cd}(\text{NH}_3)_4]^{++}$ .** A blue solution indicates Cu. If there is any doubt, acidify a portion of the solution with  $\text{HAc}$ , and add 1 drop of  $\text{K}_4\text{Fe}(\text{CN})_6$  solution. A reddish precipitate indicates Cu.

If the ammoniacal solution is blue, decolorize with  $\text{NaCN}$  solution and treat with  $\text{H}_2\text{S}$ . A yellow precipitate of  $\text{CdS}$  forms if Cd is present.

TABLE 3-10. PRECIPITATION OF Al, Ni, Zr, AND RARE EARTH GROUPS  
DETECTION OF Fe,  $\text{PO}_4$ , AND Ga

1. **Filtrate from Table 3-8, 1. Test for Fe and  $\text{PO}_4$ .** Take a small portion of the solution, boil to remove  $\text{H}_2\text{S}$ , add a little  $\text{HNO}_3$ , evaporate nearly to dryness, cool, add 5 ml. of 6  $N$   $\text{HCl}$ , 1 ml. of 12  $N$   $\text{HCl}$ , transfer to a separatory funnel and shake vigorously

TABLE 3-10. (Continued)

with ether to remove  $\text{FeCl}_3$ .  $\text{GaCl}_3$  and  $\text{TiCl}_3$  are also removed by the ether, but all other cations remain in the aqueous solution. Separate the two layers and remove the ether by evaporating each solution separately on the steam bath. To the residue from the ether solution, add a little  $\text{HCl}$ , dilute and test for  $\text{Fe}$  with  $\text{KCNS}$ . Test the evaporated aqueous layer for  $\text{H}_3\text{PO}_4$  with  $\text{HNO}_3$  and  $(\text{NH}_4)_2\text{MoO}_4$ .

Expel  $\text{H}_2\text{S}$  by boiling the remainder of the solution from Table 3-8, add liquid  $\text{Br}_2$  in slight excess and remove the excess by boiling. Add 4 ml. of 6  $N$   $\text{NH}_4\text{OH}$  and 15 ml. of 3  $N$   $\text{NH}_4\text{Ac}$ . Boil for 2 minutes. No precipitate shows absence of appreciable quantities of  $\text{Fe}$ ,  $\text{Al}$ ,  $\text{Ga}$ ,  $\text{Ti}$ , and  $\text{Zr}$ .

Cool, add 3  $N$   $\text{Fe}(\text{NO}_3)_3$  in small portions until the mixture is red and add 3 ml. in excess. Boil 2 minutes. If the precipitate does not coagulate, add 2 ml. of 6  $N$   $\text{NH}_4\text{OH}$  and boil again. Filter while hot and wash with hot water. If the filtrate shows the brownish-red color due to  $\text{Fe}$ , add more  $\text{NH}_4\text{OH}$  and then  $\text{HAc}$  to acid reaction, and boil again to effect complete precipitation.

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2. Precipitate from 1:  $\text{Fe}$ ,  $\text{Ga}$ ,  $\text{Cr}$ ,  $\text{V}$ ,  $\text{W}$ ,  $\text{Al}$ ,  $\text{In}$ ,  $\text{Zr}$ ,  $\text{Ti}$ ,  $\text{PO}_4$ , and possibly some  $\text{Zn}$ ,  $\text{Co}$ ,  $\text{Ni}$ ,  $\text{Be}$ , and  $\text{U}$  if the pH value of the solution was too high, also rare earths when  $\text{PO}_4$  is present. Dissolve in a little 6  $N$   $\text{HCl}$ , evaporate to small volume, add 10 ml. of 6  $N$   $\text{HCl}$ , and shake with an equal volume of ether that has been itself shaken with twice as much of 6  $N$   $\text{HCl}$ . Separate the layer and shake with another portion of ether.

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3. Ether layer from 2:  $\text{FeCl}_3$  and  $\text{GaCl}_3$ . Evaporate to 1 ml., add 10 ml. of 6  $N$   $\text{HCl}$ , heat to  $70^\circ$ , and shake in a small flask with 1 ml. of  $\text{Hg}$  for 5 minutes to reduce the  $\text{FeCl}_3$  to  $\text{FeCl}_2$ , which is not removed from aqueous solution by shaking with ether. Filter and reject the residue. Shake with ether again. Aqueous layer:  $\text{FeCl}_2$ . Reject.

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4. Ether layer from 3:  $\text{GaCl}_3$  and possibly some  $\text{FeCl}_3$ . Wash the ether solution by shaking with 3 ml. of 6  $N$   $\text{HCl}$  and a drop of  $\text{Hg}$ . Drain off the  $\text{Hg}$  and aqueous solution. Evaporate off ether on the steam bath, add 5 ml. of water, 2 ml. of 6  $N$   $\text{NaOH}$  to form  $\text{Na}_2\text{GeO}_2$  and  $\text{Fe}(\text{OH})_3$ . Boil, cool, add 15 ml. of water, filter, and to the solution add  $\text{HAc}$  in slight excess and boil 10 minutes. A white precipitate is  $\text{Ga}(\text{OH})_3$ . Filter and pour 3 ml. of 6  $N$   $\text{HCl}$  through the filter. Add 5 ml. of water and 3 ml. of  $\text{K}_4\text{Fe}(\text{CN})_6$  solution. A white precipitate is  $\text{Ga}_4[\text{Fe}(\text{CN})_6]_3$ .

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5. Aqueous layer from 2:  $\text{Cr}$ ,  $\text{V}$ ,  $\text{W}$ ,  $\text{Al}$ ,  $\text{In}$ ,  $\text{Zr}$ ,  $\text{Ti}$ ,  $\text{PO}_4$ ,  $\text{Zn}$ ,  $\text{Co}$ ,  $\text{Ni}$ ,  $\text{Be}$ ,  $\text{V}$ , and rare earths. Evaporate with  $\text{HNO}_3$  almost to dryness, to remove all chloride, add 10 ml. of water and 6  $N$   $\text{NaOH}$  to basic reaction. Add  $\text{Na}_2\text{O}_2$  cautiously to the cold solution.

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6. Precipitate from 5: Zirconium group:  $\text{In}$ ,  $\text{Zr}$ ,  $\text{Ti}$  as hydroxides. Also rare earths,  $\text{Co}$ ,  $\text{Ni}$ , and possibly some  $\text{Zn}$ . Analyze by Table 3-14, 1.

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7. Filtrate from 5: Aluminum group:  $\text{Cr}$ ,  $\text{U}$ ,  $\text{V}$ ,  $\text{W}$ ,  $\text{Al}$ ,  $\text{Be}$ , and  $\text{Zn}$  as  $\text{Na}$  salts, also some  $\text{Na}_3\text{PO}_4$ . Analyze by Table 3-13.

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8. Filtrate from 1:  $\text{Mn}$ ,  $\text{Zn}$ ,  $\text{Cr}$ ,  $\text{Ni}$ ,  $\text{U}$ ,  $\text{Be}$ , rare earths, alkaline earths, alkali metals, and possibly some  $\text{Cr}$ . Make ammoniacal and saturate with  $\text{H}_2\text{S}$ . Heat nearly to boiling and filter.

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TABLE 3-10. (Continued)

9. Precipitate from 8: Be, rare earths, and Cr as hydroxides. Mn, Zn, Co, Ni, and U as sulfides. Dissolve the precipitate in a little  $N$   $\text{HNO}_3$ , heat to boiling, and if there is any black residue of NiS or CoS, add a little  $16\ N$   $\text{HNO}_3$  and heat. Filter, evaporate, dilute, and treat the cooled solution with NaOH and  $\text{Na}_2\text{O}_2$  as in (5), filter and unite the filtrate with that obtained in (5).

10. Precipitate from 9: Mn, Co, Ni; Sc, Th, Ce, La, Pr, Nd, Sm, Y, Eu-Lu, and possibly Zn. Analyze by Table 3-14, 5.

11. Filtrate from 8: Alkaline earths and alkalis. Analyze by Table 3-11 and Table 3-12.

TABLE 3-11. ANALYSIS OF THE ALKALINE EARTHS

1. Filtrate from Table 3-10, 11: The alkaline earth and alkali metals. Evaporate to dryness, and heat until no more fumes are evolved. Cool, add 10 ml. water, and heat to boiling. Filter, and to cold filtrate add 15 ml.  $6\ N$   $(\text{NH}_4)_2\text{CO}_3$  reagent and 15 ml. of alcohol. Add more  $(\text{NH}_4)_2\text{CO}_3$  if necessary for complete precipitation. Allow to stand 30 minutes, filter, wash with  $(\text{NH}_4)_2\text{CO}_3$  reagent.

2. Precipitate from 1:  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ . Dissolve in small portions of  $6\ N$  HAc, and evaporate to dryness. Do not overheat residue. Dissolve residue by adding 2 ml.  $6\ N$  HAc, 10 ml.  $3\ N$   $\text{NH}_4\text{Ac}$ , and 10 ml. water. Heat to boiling; add hot  $3\ N$   $\text{K}_2\text{CrO}_4$  dropwise to complete precipitation. Boil 2 minutes and filter.

3. Filtrate from 1: The alkali metals. Analyze by Table 3-12.

4. Precipitate from 2:  $\text{BaCrO}_4$ . Dissolve in 5 ml. hot  $6\ N$  HCl, evaporate solution just to dryness, and again treat as above with HAc,  $\text{NH}_4\text{Ac}$ , and  $\text{K}_2\text{CrO}_4$ . A yellow precipitate indicates Ba.

5. Filtrate from 2: Sr, Ca, and Mg. Add  $\text{NH}_4\text{OH}$  until color changes from orange to yellow, and then 5 ml. more. Heat to  $65^\circ\text{C}$ . and add 15 ml. of alcohol. Cool and let stand. Add more  $\text{K}_2\text{CrO}_4$  and alcohol if necessary for complete precipitation of Sr. Filter.

6. Precipitate from 5:  $\text{SrCrO}_4$ . Treat with 10 ml. boiling water, add exactly 1 ml.  $3\ N$   $\text{Na}_2\text{CO}_3$  and 12 ml.  $3\ N$   $\text{K}_2\text{C}_2\text{O}_4$ . Boil gently 5 minutes, and filter hot. Discard the filtrate. Wash the precipitate and dissolve in 5 ml. cold  $N$  HAc. Add 2 ml.  $N$   $\text{Na}_2\text{SO}_4$ , heat to boiling and let stand 10 minutes. A white precipitate indicates Sr.

7. Filtrate from 5: Ca and Mg. Dilute with 50 ml. of water, add just 3 ml. of  $3\ N$   $\text{K}_2\text{C}_2\text{O}_4$  and let stand 15 minutes. If no precipitate forms, proceed to step 9, this table. If a precipitate forms, additional  $\text{K}_2\text{C}_2\text{O}_4$  is added if necessary for complete precipitation. Filter and wash with hot water.

8. Precipitate from 7:  $\text{CaC}_2\text{O}_4$ . Dissolve in 5 ml.  $6\ N$   $\text{H}_2\text{SO}_4$  and add 20 drops of alcohol. A white precipitate is  $\text{CaSO}_4$ .

TABLE 3-11. (Continued)

9. **Filtrate from 7: Mg.** Add 15 ml. 15 *N*  $\text{NH}_4\text{OH}$  and 25 ml. *N*  $\text{Na}_2\text{HPO}_4$ . Cool and let stand 30 minutes. Filter and discard the filtrate. Wash the precipitate once with alcohol. Dissolve the precipitate in 5 ml. 2 *N*  $\text{H}_2\text{SO}_4$ , add 20 ml. of alcohol and stir. Filter and discard any precipitate. Repeat the precipitation of Mg with  $\text{Na}_2\text{HPO}_4$ .

TABLE 3-12. ANALYSIS OF THE ALKALI METALS

1. **Removal of  $\text{NH}_4^+$ :** After removal of all other cations, evaporate solution to dryness, and heat with a moving flame until no more fumes are evolved. Avoid high temperature. Cool, add 5 ml. water and 1 drop of  $\text{NH}_4\text{OH}$ . Filter, and discard any residue.

2. **Removal of  $\text{SO}_4^{2-}$ :** To filtrate from 1, add 1–3 ml. concentrated  $\text{HNO}_3$  and evaporate to dryness. Ignite residue gently. Cool, add 5–10 ml. water, and then add dropwise *N*  $\text{Pb}(\text{NO}_3)_2$  until precipitation is complete. Let stand, filter, wash, and discard the precipitate. Saturate filtrate with  $\text{H}_2\text{S}$ , heat, filter, and discard the precipitate.

3. **Removal of K, Rb, and Cs:** To the filtrate from 2, add 1–5 ml. 9 *N*  $\text{HClO}_4$  and evaporate cautiously to fumes of  $\text{HClO}_4$ . Enough reagent should be added to combine with all alkali metals present. Cool, and transfer to a small dry flask with four times as much 99% alcohol as  $\text{HClO}_4$  used. Cool, shake, and let stand 15 minutes. Filter through a dry filter into a dry flask. Wash with 2 ml. 99% alcohol.

4. **Precipitate from 3:** Dissolve perchlorate precipitate in a little hot water and evaporate to dryness. To the residue add 3–12 ml. *M*  $\text{Na}_3\text{Co}(\text{NO}_2)_6$  which has been mixed with half as much 6 *N*  $\text{HAc}$ . Allow to stand 10–15 minutes with stirring and filter. Wash the precipitate with 5–10 ml. of the reagent diluted with 10 ml. of water. To washed precipitate add 1 ml. 9 *N*  $\text{NaNO}_2$ , evaporate to dryness, and ignite gently until effervescence ceases. Cool, and add 5–10 ml. of water. Filter and reject the residue. Add dropwise 6 *N*  $\text{HAc}$  until the solution is no longer basic to litmus. Filter. Reject the residue.

5. **Filtrate from 4:** To the solution add one-sixth its volume of 4 *N*  $\text{Bi}(\text{NO}_3)_3$  in 6 *N*  $\text{HAc}$ . Shake, and let stand 15–30 minutes in ice water. Warm to 30°C. and stir frequently for an additional 5 minutes. Filter.

6. **Precipitate from 5. Cs and Rb:** Dissolve precipitate in 3 ml. 6 *N*  $\text{HCl}$ , boil a few minutes, cool, and add 10 drops of 6 *M*  $\text{SbCl}_3$  in 6 *N*  $\text{HCl}$ . Let stand 30 minutes with stirring. Filter and reject precipitate. To the filtrate, add 15 ml. water and saturate with  $\text{H}_2\text{S}$ . Filter and discard precipitate. Evaporate filtrate to dryness, add 2 ml. of water, again saturate with  $\text{H}_2\text{S}$ , and filter. Evaporate filtrate carefully to dryness, cool, and add 5 drops of saturated  $\text{NaHC}_4\text{H}_4\text{O}_6$  solution. Let stand 5 minutes with stirring, then add 5 ml. more of tartrate solution. Let stand 10 minutes. A white precipitate is  $\text{RbHC}_4\text{H}_4\text{O}_6$ . Filter.

7. **Precipitate from 6:** Through filter containing  $\text{RbHC}_4\text{H}_4\text{O}_6$  precipitate, pour 0.5–5 ml. 9 *N*  $\text{NaNO}_2$  solution. Add 3–30 drops  $\text{Bi}(\text{NO}_3)_3$  reagent (4 *N*  $\text{Bi}(\text{NO}_3)_3$  in 6 *N*  $\text{HAc}$ ), shake, and let stand 30 minutes in ice water. A yellow precipitate is  $\text{Rb}_2\text{NaBi}(\text{NO}_2)_6$ .

TABLE 3-12. (Continued)

8. Filtrate from 6: Add 3 ml. of *M* silicotungstic acid reagent. Let stand 30 minutes. A fine white precipitate is  $\text{Cs}_3\text{SiW}_{12}\text{O}_{42}$ .

9. Filtrate from 5: K. Add 1 drop 0.3 *N*  $\text{Co}(\text{NO}_2)_2$  and heat to  $35^\circ\text{C}$ . for 10 minutes. Cool in ice water, let stand one hour, filter, and reject precipitate. To filtrate, add 0.5 ml. 6 *N* HAc, 2 ml. water, 0.2–2 ml. 3 *N*  $\text{Co}(\text{NO}_2)_2$ . Let stand 30 minutes. A yellow precipitate is  $\text{K}_2\text{NaCo}(\text{NO}_2)_6$ .

10. Filtrate from 3: Li and Na. Saturate the filtrate from 3 with dry HCl gas while cooling the flask in ice water. Let stand 30 minutes and filter through a small dry filter. Wash the precipitate with not more than 5 ml. 99% alcohol that has been saturated with dry HCl. At once add to the filtrate one-fourth its volume of water.

11. Precipitate from 10: NaCl. Dissolve in 5 ml. of water, and add 1 ml. 95% alcohol and 5 ml. magnesium uranyl acetate reagent. A greenish-yellow precipitate indicates Na.

12. Filtrate from 10: LiCl. Evaporate on a steam bath until the volume is equal to that of the  $\text{HClO}_4$  used in step 3 of this table. Cool, and add concentrate  $\text{HNO}_3$ , very slowly, and dropwise, until there is no further action. Then add 1 ml. concentrated  $\text{HNO}_3$  in excess and heat on a steam bath 15 minutes. Add 1 ml. more of concentrated  $\text{HNO}_3$  and heat on a wire gauze until all  $\text{HClO}_4$  is volatilized. Finally, heat for 1–2 minutes over a free flame to a temperature below redness. Cool, add 3 ml. 95% alcohol and 2 drops concentrated  $\text{NH}_4\text{OH}$ . Filter, and discard any residue. To the filtrate add 3 ml. concentrated  $\text{NH}_4\text{OH}$ , heat to  $35\text{--}40^\circ\text{C}$ ., and add 2 drops of 0.5 *N*  $\text{Na}_2\text{HPO}_4$ . Shake. A precipitate indicates Li.

TABLE 3-13. ANALYSIS OF THE ALUMINUM GROUP

1. Filtrate from Table 3-10, 7: Cr, U, V, W,  $\text{PO}_4$ , Al, Zn, and Be as Na salts. Add 6 *N*  $\text{HNO}_3$ , which has been freed from  $\text{HNO}_2$  by boiling 1 minute in a test tube, until the solution is acid to litmus. Dilute to 100 ml. in a 250-ml. bottle, add solid  $\text{NaHCO}_3$  until the solution is practically neutral to litmus and add 1.5 g. in excess. Add 1 ml. of *M*  $\text{H}_2\text{O}_2$  solution, stopper the bottle, and heat in gently boiling water for 20 minutes. Cool carefully and filter promptly.

2. Filtrate from 1:  $\text{Na}_2\text{CrO}_4$ ,  $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{Na}_3\text{VO}_4$ , and  $\text{Na}_2\text{WO}_4$ . If the solution is colorless, do not test for Cr. If colored yellow, carefully neutralize with 6 *N*  $\text{HNO}_3$ , free from  $\text{HNO}_2$ , adding 2 ml. in excess. Add 25 ml. of *N*  $\text{Pb}(\text{NO}_3)_2$ . If this test is omitted, add the  $\text{HNO}_3$  alone.

3. Precipitate from 2:  $\text{PbCrO}_4$ . Dissolve in 10 ml. of warm 1.5 *N*  $\text{HNO}_3$ . To the yellow solution, add 2 ml. of ether and a little  $\text{H}_2\text{O}_2$ . A blue ether solution contains  $\text{H}_3\text{CrO}_7$ .

4. Filtrate from 2:  $\text{UO}_2(\text{NO}_3)_2$ ,  $\text{H}_3\text{VO}_4$ ,  $\text{H}_3\text{PO}_4(\text{WO}_3)_{12}$ ,  $\text{Pb}(\text{NO}_3)_2$ . Saturate with  $\text{H}_2\text{S}$ , filter off, and reject the  $\text{PbS}$  precipitate. Evaporate to about 40 ml., cool, neutralize

TABLE 3-13. (Continued)

with  $\text{NH}_4\text{OH}$ , add 5 ml. of 6 *N*  $\text{HAc}$  and 15 ml. of *N*  $\text{Na}_2\text{HPO}_4$ . Heat to boiling, filter, and wash the precipitate with *N*  $\text{NH}_4\text{NO}_3$  solution.

5. **Precipitate from 4: White  $\text{UO}_2\text{NH}_4\text{PO}_4$ .** Dissolve this precipitate or the  $(\text{NH}_4)_2\text{U}_2\text{O}_7$  precipitate obtained in (12) in a little hot 6 *N*  $\text{HCl}$ , evaporate nearly to dryness, add 10 ml. of water containing 0.5 g. of  $\text{NaCl}$  and treat with 5 ml. of  $\text{K}_4\text{Fe}(\text{CN})_6$ . A dark red precipitate or coloration is  $\text{K}_2\text{UO}_2[\text{Fe}(\text{CN})_6]$ .

6. **Filtrate from 4:  $\text{H}_3\text{VO}_4$ ,  $\text{H}_3\text{PO}_4(\text{WO}_3)_{12}$ .** Make strongly ammoniacal and saturate with  $\text{H}_2\text{S}$ . A pink or violet-red color indicates the presence of V. Make the colored solution acid with  $\text{HNO}_3$  and heat. Filter off the precipitate.

7. **Precipitate from 6:  $\text{V}_2\text{S}_4$ -5.** Dissolve by heating with 2 ml. of 16 *N*  $\text{HNO}_3$ , add 3 ml. of water, boil and filter if necessary. Cool and add 1 ml. of  $\text{H}_2\text{O}_2$  solution. An orange-red color is due to  $\text{HVO}_4$ . Evaporate to dryness, add 5 ml. of *N*  $\text{NH}_4\text{OH}$  and 1-2 ml. of *N*  $\text{NH}_4\text{OH}$  which is saturated with  $\text{NH}_4\text{Cl}$ . If a precipitate forms, add 2 ml. of water and mix. A white precipitate is  $\text{NH}_4\text{VO}_3$ .

8. **Filtrate from 6:  $\text{H}_3\text{PO}_4(\text{WO}_3)_{12}$ .** If phosphate was found in Table 3-10, 1, make the filtrate slightly ammoniacal, add 20 ml. of  $\text{Mg}(\text{NO}_3)_2$  reagent, boil, cool somewhat, and add 5 ml. of 15 *N*  $\text{NH}_4\text{OH}$ . After an hour, filter off and reject the precipitate of  $\text{MgNH}_4\text{PO}_4$ . Boil off  $\text{NH}_3$  from the filtrate, add 3 ml. of 16 *N*  $\text{HNO}_3$ , evaporate to 10 ml., add 1 ml. more of  $\text{HNO}_3$  and 5 ml. of water. Heat until all crystalline salts have dissolved. A white or yellow residue is probably tungstic acid. Test for W as in Table 3-4, 7.

9. **Precipitate from 2:  $\text{Al}(\text{OH})_3$ ,  $\text{ZnCO}_3$ ,  $\text{BeCO}_3$ ,  $(\text{UO}_2)_3(\text{VO}_4)_2$ .** Dissolve the precipitate in 10 ml. of hot 6 *N*  $\text{HCl}$ , catching the solution in a small flask. Cool, add 15 ml. of ether, and introduce dry  $\text{HCl}$  gas until there is no line of demarcation between the ether and aqueous acid, keeping the ether cold. Filter through asbestos, and wash with a mixture of 2 volumes 12 *N*  $\text{HCl}$  and 3 volumes of ether which has been saturated with  $\text{HCl}$  gas.

10. **Precipitate from 9:  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ .** Dissolve in a little  $\text{HCl}$ , precipitate with  $\text{NH}_4\text{OH}$ , and dissolve the precipitate in 5 ml. *N*  $\text{HCl}$ . Add 5 ml. 3 *N*  $\text{NH}_4\text{Ac}$  and 5 ml. of 0.1% aqueous aluminon solution, and make basic with a mixture of  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$ . A bright red precipitate indicates aluminum.

11. **Filtrate from 9:  $\text{ZnCl}_2$ ,  $\text{BeCl}_2$ ,  $\text{UO}_2\text{Cl}_2$ ,  $\text{VOCl}_2$ .** Evaporate off the ether on the steam bath until the volume is reduced to 2 ml., add 20 ml. of water, and make ammoniacal. Heat to boiling and filter.

12. **Precipitate from 11:  $\text{Be}(\text{OH})_2$ ,  $(\text{NH}_4)_2\text{U}_2\text{O}_7$ ,  $\text{VO}(\text{OH})_2$ .** (Possibly some  $\text{Zn}(\text{OH})_2$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_3$  and  $\text{H}_2\text{SiO}_3$ .) Pour hot 6 *N*  $\text{HAc}$  through the filter to dissolve the precipitate. Evaporate the solution just to dryness, triturate the dry residue with 10 ml. of dry chloroform, and filter through a dry filter.

13. **Solution from 12:  $\text{BeO} \cdot 3\text{BeAc}_2$ .** Wash the chloroform solution in a separatory funnel with 10 ml. of water, evaporate off the chloroform, and dissolve the basic beryllium

TABLE 3-13. (Continued)

acetate in a little 6 *N* HNO<sub>3</sub>, dilute and add NH<sub>4</sub>OH in slight excess. A white flocculent precipitate is Be(OH)<sub>2</sub>.

14. Residue from 12: U, V, Al, Fe, Zn, Be, etc. To the residue add 25 ml. of 1% NaHCO<sub>3</sub>, boil, and filter. Reject the residue.

15. Solution from 14: Na<sub>4</sub>UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>. Test for U as in (5) of this table.

16. Filtrate from 11: [Zn(NH<sub>3</sub>)<sub>4</sub>]<sup>++</sup>. Acidify with HAc and saturate with H<sub>2</sub>S. Filter, and dissolve the precipitate in a little HNO<sub>3</sub>. Add 1–3 drops of 0.3 *N* Co(NO<sub>3</sub>)<sub>2</sub> solution, evaporate to dryness, and ignite until the purple color of the Co salt disappears. A green residue indicates zinc.

TABLE 3-14. ANALYSIS OF THE NICKEL AND ZIRCONIUM GROUPS  
ISOLATION OF THE RARE EARTH GROUP

1. Peroxide precipitate from Table 3-10, 6: Mn(Zn), Co, Ni, and rare earths as hydroxides. Dissolve in 5 to 20 ml. of 6 *N* HCl, heating gently. Filter if necessary. Add 3 ml. of 15 *N* HNO<sub>3</sub> and evaporate to about 1 ml. Add 15 ml. of 15 *N* HNO<sub>3</sub> and 1 g. powdered KClO<sub>3</sub>, and heat to boiling. Add an additional 10 ml. HNO<sub>3</sub>, heat to boiling, remove the flame, and add 0.5 g. KClO<sub>3</sub>. Repeat this treatment until about 3 g. of KClO<sub>3</sub> have been added. Caution: *do not add the chlorate to the boiling solution!*

2. Precipitate from 1: MnO<sub>2</sub>. Dissolve the MnO<sub>2</sub> in a little hot 6 *N* HNO<sub>3</sub> and a few drops H<sub>2</sub>O<sub>2</sub>. Boil and cool to room temperature. Add a little solid NaBiO<sub>3</sub>. A purple color indicates Mn.

3. Filtrate from 1: Ni, Co, Zn, and rare earths as nitrates. Evaporate to small volume, add 30 ml. of cold water and a slight excess of NH<sub>4</sub>OH. If there is no precipitation, rare earths are absent. In such cases, saturate with H<sub>2</sub>S and examine the resulting precipitate for Ni, Co, and Zn by Table 3-15.

If NH<sub>4</sub>OH gives a precipitate, add 3 ml. of 6 *N* HAc, filter if a precipitate remains, and unite it with the NH<sub>4</sub>OH precipitate to be obtained in (5). To the clear solution, add 10 ml. of 3 *N* NH<sub>4</sub>Ac solution, heat to 75°, and saturate with H<sub>2</sub>S. Filter

4. Precipitate from 3: ZnS, CoS, NiS. Analyze by Table 3-15.

5. Filtrate from 3: Rare earths. Expel H<sub>2</sub>S by boiling and reject any precipitate that may form. Make distinctly ammoniacal, filter, and reject the filtrate. Combine this precipitate with the residue from the acetic acid treatment of (3) and with the peroxide precipitate from Table 3-10, 10, dissolve in 10 ml. of 6 *N* HCl, and evaporate nearly to dryness. Transfer to a platinum dish, evaporate to dryness of a water bath, add 2 ml. of water, 1 ml. of 6 *N* HCl, about 0.5 ml. of HF, and 9 ml. of water. Use more HF if the residue is large. Heat on a steam bath for 5 minutes and filter through a plastic funnel into another platinum dish.

6. Precipitate from 5: Fluorides of rare earths and possibly In. Examine by Table 3-16.

TABLE 3-14. (Continued)

7. **Filtrate from 5: Fluorides of In, Zr, Ti and possibly Ni, Co, and Zn.** Neutralize with  $\text{NH}_4\text{OH}$ , make slightly acid with  $\text{HF}$ , and saturate with  $\text{H}_2\text{S}$ . Filter through a plastic funnel into a platinum dish. If much precipitate forms, boil the filtrate to expel  $\text{H}_2\text{S}$  and repeat the treatment with  $\text{NH}_4\text{OH}$ ,  $\text{HF}$ , and  $\text{H}_2\text{S}$ .
- 
8. **Precipitate from 7:  $\text{In}_2\text{S}_3$ , ( $\text{ZnS}$ ,  $\text{CoS}$ ,  $\text{NiS}$ ).** A pale yellow precipitate is  $\text{In}_2\text{S}_3$ . Dissolve in 5 ml. of 6  $N$   $\text{HCl}$ , adding  $\text{HNO}_3$  if necessary to dissolve any black  $\text{NiS}$  or  $\text{CoS}$ . Boil to expel  $\text{H}_2\text{S}$ , add an excess of  $\text{NH}_4\text{OH}$ , and filter. Reject the filtrate.
- 
9. **Precipitate from 8:  $\text{In}(\text{OH})_3$ .** Dissolve in 10 ml. of hot, 6  $N$   $\text{HAc}$  and saturate with  $\text{H}_2\text{S}$ . A deep yellow precipitate is  $\text{In}_2\text{S}_3$ .
- 
10. **Filtrate from 7:  $\text{H}_2\text{ZrF}_6$ ,  $\text{H}_2\text{TiF}_6$  ( $\text{CoF}_2$ ,  $\text{NiF}_2$ ).** Add 3 ml. of concentrated  $\text{H}_2\text{SO}_4$  and evaporate to fumes. Cool, add water, and test with  $\text{H}_2\text{O}_2$  and  $\text{Na}_2\text{HPO}_4$  for Zr and Ti as in Table 3-5.
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TABLE 3-15. ANALYSIS OF COBALT, NICKEL, AND ZINC

1. **Sulfide precipitate from Table 3-14, 4:  $\text{CoS}$ ,  $\text{NiS}$ ,  $\text{ZnS}$ .** Treat precipitate with 10-30 ml. cold 1  $N$   $\text{HCl}$ . Filter.
- 
2. **Residue from 1:  $\text{CoS}$ ,  $\text{NiS}$ .** Dissolve in 5-15 ml. 6  $N$   $\text{HCl}$ , heat to boiling, and add a little powdered  $\text{KClO}_3$ . Filter, and evaporate the solution to dryness. Dissolve residue in 5 ml. 6  $N$   $\text{HAc}$  and add 3 ml. 6  $N$   $\text{KNO}_2$ . Let stand 15 minutes. A yellow precipitate of  $\text{K}_3\text{Co}(\text{NO}_2)_6$  indicates Co. Filter.  
To the filtrate, add dimethylglyoxime. A red precipitate indicates Ni.
- 
3. **Filtrate from 1: Zn (traces of Co and Ni).** Carefully neutralize with  $\text{NaOH}$  and add a little solid  $\text{Na}_2\text{O}_2$ . Filter.
- 
4. **Precipitate from 3:  $\text{Co}(\text{OH})_3$  and  $\text{Ni}(\text{OH})_3$ .** Add to the residue of  $\text{NiS}$  and  $\text{CoS}$ , step 2 of this table.
- 
5. **Filtrate from 3:  $\text{HZnO}_2^-$ .** Acidify, treat with  $\text{H}_2\text{S}$ , and confirm Zn as described in Table 3-13, 16.
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TABLE 3-16. ANALYSIS OF RARE EARTH GROUP

1. **Precipitate from Table 3-14, 6: Fluorides of Sc, In, and rare earths.** Treat with 10 ml. of 6  $N$   $\text{NH}_4\text{OH}$  and half as much 27  $N$   $\text{HF}$  in a platinum dish. Heat near the boiling point for 3 minutes and filter through a plastic funnel into another platinum dish.
- 
2. **Residue from 1: Rare earth and In fluorides.** Transfer the fluoride precipitate to a platinum dish, add 2 ml. of concentrated  $\text{H}_2\text{SO}_4$ , and evaporate to strong fumes of  $\text{H}_2\text{SO}_4$ . Cool, pour into 25 ml. of water, and make ammoniacal. Filter and reject the filtrate. Dissolve the hydroxide precipitate in 5 ml. of 6  $N$   $\text{HAc}$  and saturate with  $\text{H}_2\text{S}$ . A yellow precipitate is  $\text{In}_2\text{S}_3$ .
-

TABLE 3-16. (Continued)

**3. Filtrate from 2: Rare earth acetates.** Boil off  $\text{H}_2\text{S}$ , evaporate just to dryness, add 6 ml. of 16  $N$   $\text{HNO}_3$  and 1 g. of powdered  $\text{KClO}_3$ . Heat 5 minutes on the steam bath with the dish covered. Add 20 ml. of cold 7.5%  $\text{KIO}_3$ . Cool to  $20^\circ$  and filter, washing the precipitate with cold, 1%  $\text{KIO}_3$  solution.

**4. Precipitate from 3:  $\text{Th}(\text{IO}_3)_4$ ,  $\text{Ce}(\text{IO}_3)_4$ .** Rinse the precipitate into a small Erlenmeyer flask and digest with 18 ml. of  $M$   $\text{H}_2\text{O}_2$  and 5 ml. of 16  $N$   $\text{HNO}_3$ , using double these quantities if the precipitate is large. Add 0.75 g. of  $\text{KIO}_3$  dissolved in 10 ml. of water, and allow to stand for some time. Filter and wash with 1%  $\text{KIO}_3$  solution.

**5. Residue from 4:  $\text{Th}(\text{IO}_3)_4$ .** Dissolve in hot 6  $N$   $\text{HCl}$ , evaporate to dryness, moisten with 12  $N$   $\text{HCl}$  and dry until no odor of  $\text{HCl}$  remains. This serves to decompose and reduce all  $\text{IO}_3^-$ . Dissolve the residual  $\text{ThCl}_4$  in 2 ml. of water and add 2 drops of 6  $N$   $\text{HCl}$  and 5 ml. of  $\text{H}_2\text{O}_2$  solution. A white precipitate is  $\text{ThO}_2 \cdot \text{H}_2\text{O}$ .

**6. Solution from 4:  $\text{Ce}(\text{IO}_3)_3$ .** Make ammoniacal and heat to boiling. A yellow or orange precipitate is  $\text{CeO}_2 \cdot \text{H}_2\text{O}$ .

**7. Filtrate from 3: Other rare earths.** Make ammoniacal, filter off the rare earth hydroxides, and discard the filtrate. Wash the precipitate with hot water and dissolve it in 5–10 ml. of 6  $N$   $\text{HCl}$ . Evaporate to dryness, moisten with 12  $N$   $\text{HCl}$ , and dry on the water bath. To the dry residue, add exactly 3 ml. of 50%  $\text{K}_2\text{CO}_3$  solution, heat in a covered dish for two hours on the steam bath, replacing water lost by evaporation. Filter.

**8. Precipitate from 7: Lanthanum group: La, Pr, and most of the Nd, Sm, and Eu** with small quantities of the yttrium group, all as double carbonates of K. Dissolve in 5–10 ml. of 6  $N$   $\text{HNO}_3$  dilute with water to 25 ml., and boil. This serves to precipitate the La group as hydroxides.

Unite this precipitate of lanthanum earth hydroxides with the similar precipitate obtained in (14). Dissolve in 5–10 ml. of 6  $N$   $\text{HNO}_3$ , evaporate to dryness in a porcelain crucible, mix with 2 drops of 6  $N$   $\text{HNO}_3$ , 2 drops of water and 7 g. of  $\text{NaNO}_3$ . Heat 5 hours at  $445^\circ$ ; this serves to convert nearly all of the Pr as brown  $\text{PrO}_2$ . Cool and extract the melt with cold water.

**9. Residue from 8:** Transfer the impure  $\text{PrO}_2$  precipitate to a flask with 20 ml. of  $N$   $\text{NaAc}$  and 4 ml. of  $N$   $\text{HAc}$ . Shake occasionally for 10 minutes and filter.

**10. Residue from 9:  $\text{PrO}_2$  with some  $\text{La}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$ .** If the residue is very dark colored, do not treat it further. Otherwise dissolve in 5 ml. of hot, 6  $N$   $\text{HCl}$ . Add 5 ml. of water and make ammoniacal. A light green precipitate is probably  $\text{Pr}(\text{OH})_3$  and will change to brown  $\text{PrO}_2$  on ignition.

**11. Solution from 9.** Make the acetate solution basic with  $\text{NH}_4\text{OH}$ . If a precipitate forms, rare earths are present. If the residue (10) was dark colored, discard this hydroxide precipitate. Otherwise filter it off and ignite in an open crucible. A chocolate brown residue contains  $\text{PrO}_2$ .

TABLE 3-16. (Continued)

**12. Water Extract from 8: Most of the La with some Nd and Sm.** Make slightly ammoniacal, filter off the rare earth hydroxide, and reject the filtrate of sodium salts. Dissolve in 50%  $\text{K}_2\text{CO}_3$  solution using 1 ml. for each mg. of precipitate. Add 8 times as much water and heat in nickel or platinum for 2 hours on the steam bath. A white flocculent precipitate is  $\text{KLa}(\text{CO}_3)_2$ . Filter it off, ignite the precipitate in a porcelain crucible, and add 2 drops of 6 *N*  $\text{HNO}_3$ . A white residue confirms the presence of La; if the double carbonate contained Pr, brown  $\text{PrO}_2$  would be formed. Filter, add  $\text{HCl}$ , boil off  $\text{CO}_2$ , and add  $\text{NH}_4\text{OH}$ ; a precipitate indicates Nd, Sa, or the yttrium group.

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**13. Filtrate from 7: Yttrium group: Gd, Tb, Dy, Ho, Er, Tu, Yb, and Y with small quantities of the lanthanum group, especially Nd, Sm, and Eu.** Add  $\text{HCl}$  in slight excess, boil off  $\text{CO}_2$ , and make basic with  $\text{NH}_4\text{OH}$ . Filter and reject the filtrate.

Dissolve the precipitate in 5–10 ml. of 6 *N*  $\text{HCl}$ , evaporate to dryness, moisten with 12 *N*  $\text{HCl}$ , and dry until no odor of  $\text{HCl}$  remains. To the residue, add just 1.5 ml. of 90%  $\text{HCO}_2\text{H}$ . Shake well, transfer to a test tube, boil, cool, and let stand 10 minutes. Filter and wash with a mixture of 0.3 ml.  $\text{HCO}_2\text{H}$  and 1 ml. of 6 *N*  $\text{NH}_4\text{OH}$ .

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**14. Precipitate from 13: A crystalline precipitate may contain Nd, Sa, or Eu as formate.** Dissolve in 5–10 ml. of 6 *N*  $\text{HNO}_3$ , dilute to 25 ml., make ammoniacal, and heat to boiling. Filter off the rare earth hydroxides, using the same filter as that used to filter off a similar precipitate obtained in (8) and fuse with  $\text{NaNO}_3$  as there directed.

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**15. Filtrate from 13: The Yt group of rare earths.** Dilute to 25 ml., make ammoniacal, and boil. A white or reddish-white precipitate shows the presence of the yttrium group, the separation of which is so difficult and tedious that it will not be discussed here.

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**16. Solution from 15:  $\text{NH}_4\text{ScF}_4$ .** Add 2 ml. of concentrated  $\text{H}_2\text{SO}_4$  and evaporate to dense fumes. If Sc is present, it is left in the strongly fumed acid as a white translucent mass. If such a residue is visible, dissolve it in 10 ml. of water, and precipitate  $\text{Sc}(\text{OH})_3$  by adding  $\text{NH}_4\text{OH}$ . Dissolve the  $\text{Sc}(\text{OH})_3$  precipitate in 5 ml. of 6 *N*  $\text{HCl}$ , evaporate to dryness in a platinum dish, add 4–5 drops of water and a drop of  $\text{HF}$ . A white precipitate of  $\text{ScF}_3$ , soluble in excess  $\text{HF}$ , shows Sc to be present.

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# THE RING OVEN METHOD

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The *Ring Oven* method<sup>5</sup> was originally developed to carry out chemical separations in one single drop of sample solution. The ring oven (Fig. 3-1) consists essentially of a cylindrical heating block, *H*, made of aluminum (other materials have also been used: stainless steel, gold plated copper, glass,<sup>6</sup> etc.) which bears in its center a bore hole of 22-mm. inner diameter (dotted line). A heating wire is installed in this block. An adjustable resistance serves to regulate the temperature of the heating block, which should at the surface be about 110–115°C., if working with aqueous solutions. The test drop is placed in the center of a round filter (55-mm. diameter) by means of a self-filling capillary pipet (~1.5  $\mu$ l. volume).

One group of substances is precipitated in this test drop using an appropriate reagent (e.g.,  $H_2S$ ) and thus fixed locally in the fleck on the paper. The filter paper is then placed on the ring oven so that the spot lies just underneath the guiding glass tube, *G1*; this glass tube must stand vertically, point exactly to the middle of the bore hole, and end several millimeters above the surface of the heating block. The unprecipitated parts of the sample spot are then washed away from the precipitate fixed in the spot by means of a suitable solvent (water, acid, ammonium hydroxide, alcohol, etc.) applied by a capillary pipet. This washing pipet just fits into the narrow glass guiding tube, *G1*.

The substances dissolved in the applied solvent migrate outward, due to the capillary action of the filter paper, until they reach the edge of the bore hole of the hot heating block. There the solvent evaporates and the solutes are deposited in a very narrow, sharply outlined ring zone of 22-mm. diameter.

The electrical lamp, *L*, underneath the heating block, enables the washing-out procedure to be controlled more readily. The area between the initial spot and the ring zone is naturally free of sample components; consequently, the inner spot—bearing the precipitated group of the sample—can be cut out mechanically by means of a punch of proper size. The precipitate on the little disc can be treated in a suitable way, such as oxidation, and then separated further by another precipitation. Then, the little disc is placed centrally on a fresh round filter and again extracted with an appropriate solvent on the ring oven, just as though the disc were nothing but an ordinary spot on the paper.

The resulting rings have a width of about 0.1–0.3 mm.; the area of these rings is consequently much smaller than the area of the initial spot. Therefore the concentration of the washed-out substances is even greater in the ring than in the original spot.

<sup>5</sup> Weisz, H., *Mikrochim. Acta*, 1954, 140; Weisz, H., *Chem. Age*, 1954, 1039; Stephen, W. I., *Waverley Gold Medal Essay Research X*, 429, 1957.

<sup>6</sup> Balczó, H., *Mikrochim. Acta*, 1959, 314.

The filter is divided into several sectors, and on the individual sectors the various members of the corresponding group are identified by spraying with suitable reagent solutions. Sharply outlined circular arcs of the respective color appear on the sectors if the substance in question is present.

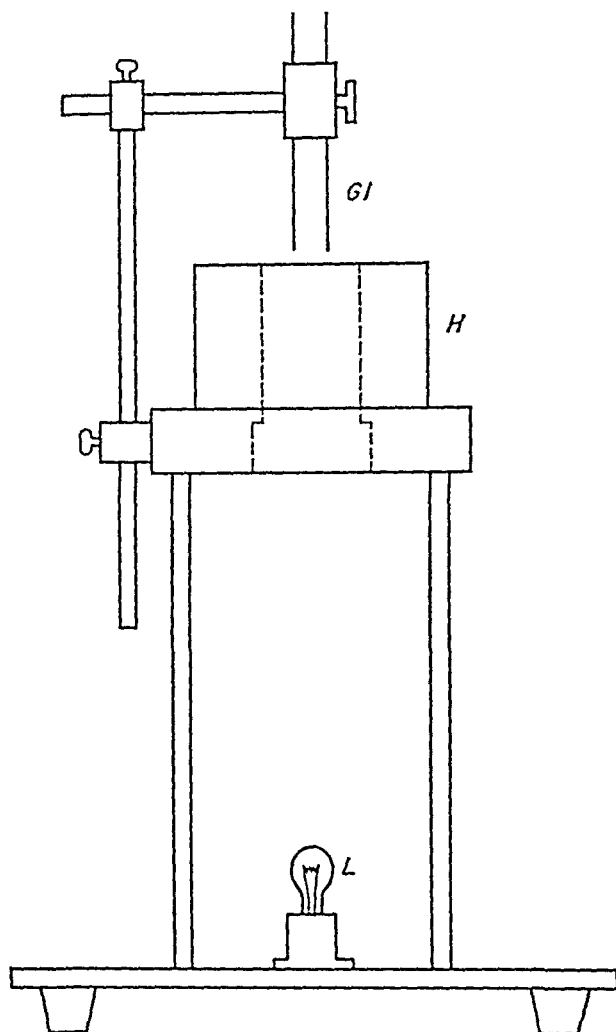


FIG. 3-1.

Several auxiliary items of equipment have been described (pipets, sample pipets, glass-holder, gas-generator, etc.).

With the aid of this method, a separation procedure for 14 metals has been worked out,<sup>7</sup> which needs only one single drop ( $1.5 \mu\text{l.}$ ) containing a few micrograms of solid test material. The metals are divided into 4 groups (3 rings and 1 spot).

A separation procedure for 35 metallic ions has also been described, which employs both liquid-liquid extraction procedures and the ring oven method.<sup>8</sup>

<sup>7</sup> Weisz, H., *Mikrochim. Acta*, 1954, 376; Bank, C. A., and van den Eijk, *Chem. Weekblad*, 51, 351, 1955.

<sup>8</sup> West, P. W., and Mukherji, A. K., *Anal. Chem.*, 31, 947, 1959.

This technique enables semiquantitative spot-colorimetric analysis; the results have only an error of  $\pm 5-8\%$ , using a total of about 2 micrograms of the respective ion.<sup>9</sup>

The ring oven method may also be employed in combination with electrographic sampling for qualitative and semiquantitative analysis of steel and alloys.<sup>10</sup>

The use of this method for the examination of tiny amounts of radioactive materials has also been described.<sup>11</sup> Combinations with paper chromatography have been worked out.<sup>8</sup>

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<sup>9</sup> Weisz, H., Mikrochim. Acta, 1954, 460, 785; Stephen, W. I., Mikrochim. Acta, 1956, 1540; Knodel, W., and Weisz, H., Mikrochim. Acta, 1957, 417; Weisz, H., Celap, M., and Almazan, V., Mikrochim. Acta, 1959, 36.  
<sup>10</sup> Stephen, W. I., Mikrochim. Acta, 1956, 1531, Nall, W. R., and Scholey, R., Metallurgia, 1956, 97.  
<sup>11</sup> Weisz, H., and Scott, F., Mikrochim. Acta, 1956, 1856.

## Chapter 4

# MECHANICAL SEPARATION

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*Introduction.*—In quantitative analysis the final determination of an element or compound is based on the physical measurement of a physical or chemical property of the substance, the magnitude of which is a function of the amount present. Before the final determination can be made the element or compound is usually separated by some mechanical method. The performance of such a chemical analysis is an art that requires the analyst to combine his knowledge of the theory of analytical chemistry with his highly developed mechanical manipulative skill. Any one who has acquired sufficient mechanical skill to perform an exact quantitative analysis can adapt to the performance of a less accurate one but the converse of this is not true.

There are several basic separations in analytical chemistry that are either completely mechanical or depend largely on a mechanical operation. The separations are: (1) solids from solids; (2) solids from liquids; (3) solids from gases; (4) liquids from liquids; (5) liquids from gases; and (6) gases from gases. In each of these separations the accuracy one obtains depends on the care with which the analyst mechanically transfers the original sample and the separated components, whether they are solids, liquids, or gases, and the efficiency of the particular mechanical separation involved.

*Separation of Solids from Solids.*—Usually the mechanical separation of solids from solids depends on the physical property of size. A weighed sample of the solid material is placed in the top compartment of a nest of sieves. The sieves are shaken for a specified length of time either by hand or by a mechanical shaker, although the latter method is preferred. The amount of material that is retained on a sieve of a specified size is collected and weighed. The sieves are available in standard sizes 10, 20, 40, 100, 200, etc., mesh, and are made of brass, steel, or plastic. For separating solids that are of subsieve size, one can use other methods, which depend on the fact that the resistance of a solid particle passing through a specified liquid or gaseous atmosphere depends on the size of the particle, and thus, the solid particles will be separated according to size.

The determination of the size of solids is extremely important to many processes. The strength of concrete, for instance, depends on the amount and size of the aggregate used. The quality of many paints depends on the size of the various pigments. The rates of chemical reactions depend on the size of the raw feed material. Many more examples could be cited.

*Separation of Solids from Liquids.*—The solid to be separated from a liquid is usually a precipitate that is formed in the solution. The exact condition for the formation of a filterable precipitate is outlined in each particular method. The principle of the actual separation is similar to that employed in the separation of solids from solids except that the sieves are replaced by filters of porous porcelain, fritted glass, sintered stainless steel, porous platinum, or filter paper.

*Filtration.*—The filtration step in analysis is of extreme importance. The quality, as well as the quantity, of an analyst's work is controlled to a large extent by his selection of the filtering medium and the filtering apparatus. The majority of filtrations are made through paper at atmospheric pressure. Quantitative filter paper is available in various degrees of fineness, and the fineness of the paper to be used is determined by the character of the precipitate. The amount of precipitate to be collected, and not the volume of liquid to be filtered, determines which of the various sizes of filter paper available should be selected. The whole precipitate should not occupy much more than one-third of the capacity of the folded filter paper.

The proper fitting of the filter paper in a funnel is an art that can be mastered only by constant practice. When properly set, the filtering paper should fit the funnel snugly at the top and its top edge should be about 10 to 15 mm. below the rim of the funnel; the paper should not touch the sides of the funnel for the rest of its length. If the paper has been properly fitted, water should pass through it rapidly, leaving the stem of the funnel full of water.

The characteristics of precipitates vary according to the type of precipitate and to the method of formation. Some are gelatinous; others are crystalline and may vary in size from very small to relatively large crystals; some have a strong tendency to creep while others may stick fast to the sides of the beakers. It is recommended that the walls of the beaker be thoroughly scrubbed with a well wetted rubber-tipped "policeman," and, in some instances, this policing should be supplemented by rubbing the sides and bottom of the beaker with a small piece of quantitative filter paper. The analyst should guard against the possibility of any precipitate escaping beyond the upper edge of the filter paper, as well as creeping down the sides of the beaker. In other words, make sure all of the precipitate is transferred from the beaker to the inside of the filter.

All precipitates are partially soluble, especially if recently produced, and proper precautions should be taken with respect to both their formation and subsequent washing. In general, precipitates should not be washed with water alone but with water containing a small amount of a common ion to decrease the solubility of the precipitate. The amount and kind of washing solution that must be used depend on the nature of the precipitate and how the precipitate is to be determined, that is, whether the precipitate is to be ignited and weighed or dissolved and titrated. Gelatinous precipitates, such as the  $R_2O_3$  group, require more washing than crystalline ones, such as magnesium ammonium phosphate. The best way to wash the precipitate and the amount and kind of washing that is required to remove any interfering substances must be determined for each new set of conditions.

*Centrifugation.*—The centrifuge can be used to great advantage in some separations of solids from liquids. It is extremely useful for washing precipitates by decantation, and for collecting difficultly filterable precipitates. It may also be used for some routine determinations by measuring the volume of the precipitate. In the latter application, however, the physical state of the precipitate is of prime impor-

tance and the procedure must be carefully worked out and strictly followed to obtain reproducible results.

**Separation of Solids from Gases.**—Numerous rocks, minerals, ores, and salts contain various amounts of gases and vapors. Many metals and alloys likewise may contain various amounts of gases. For a complete analysis of such substances, the gases must be determined. This is especially true in the analysis of metals and alloys because their properties vary according to the kind and amount of gas present.

The gas to be separated may be liberated by chemical action, as for example, the decomposition of limestone with an acid, or by physical means, such as direct heating with or without a flux, such as determining gases dissolved in steel.

Regardless of the method of its liberation, the gas must be transferred from the reaction vessel to the gas buret, if a volumetric method is used, or to a weighed absorbing system, if the gas is to be weighed, or to an absorbing liquid, if the gas is to be determined by some chemical reaction.

In transferring a gas one must employ techniques similar to those used in transferring precipitates. The transferring medium, instead of being a washing solution, is a stream of inert gas, and the sieve or filter is either a solid or liquid adsorbant that catches and retains only the desired gas. One must be certain that the gas to be determined will neither react with, nor be absorbed by, the tubes and vessels through which it is transferred from one place to another. Particular attention should be given to the types of lubricants used on stopcocks and ground glass joints. Likewise, care must be taken in the use of rubber and plastic tubing. In the actual determination, the gases must be mechanically driven by a stream of inert gas through a series of absorption media to remove interfering gases, and finally into the medium that absorbs only the gas to be determined.

**Separation of Liquids from Liquids.** The mechanical separation of liquids from other liquids depends primarily on the physical property of density, i.e., one liquid phase must float on top of the other liquid phase. In addition, the liquids to be separated must be completely immiscible in each other, or the mutual solubility of each in the other must be known, so that final analytical results can be corrected for any error. In some separations, if the two liquids are not immiscible, a third substance, which is soluble in one of the liquids, may be added to the mixture, causing the two liquids to separate into two phases. The apparatus most commonly used for such mechanical separations is the separatory funnel. Separatory funnels are available in a variety of shapes and sizes. In the separation of some liquids, a reagent may be added that reacts with one of the liquids to form a precipitate, and in this case the separation is that of a solid from a liquid.

**Separation of Liquids from Gases.**—There are several mechanical methods of separating liquids from gases. One of the most commonly used is the displacement, or sweeping out, of the gas to be determined by an inert gas; carbon dioxide, for instance, can be completely removed from distilled water by bubbling a stream of air, free from carbon dioxide, through the distilled water; similarly, oxygen can be removed by a stream of argon or other inert gas. This displacement process is very similar to the washing of a precipitate in that the stream of inert gas is the washing medium and the gas to be determined is the material that is transferred. If such gases are to be determined they must be completely transferred to an absorbing medium that absorbs only the desired gas.

**Separation of Gases from Gases.**—If the substance to be analyzed is entirely gaseous, special techniques, methods, and apparatus are used. Nevertheless, the

transfer of the material remains mechanical, and, as in other types of analysis, the accuracy obtained depends on the mechanical skill of the analyst.

In conclusion, it can be stated that some kind of mechanical separation is required in nearly every analysis, and the accuracy of the results obtained depends greatly on the skill with which the analyst performs the particular separation.

## *Chapter 5*

# SEPARATION BY PRECIPITATION

One of the most common of all methods used for the elimination of interference in an analytical procedure is based on separation by precipitation. Such reactions are used for several different reasons. The most important of these are: (a) to convert the desired substance to a suitable insoluble weighing form; (b) to precipitate the substance to be determined specifically or selectively as a preliminary to making the final determination by some other method, as titrimetrically; or colorimetrically; and (c) for the removal of interfering substances so as to leave the desired substance in solution for final determination by appropriate means.

Satisfactory precipitation is achieved in most cases as follows: (a) by changing the hydrogen ion concentration of the solution; (b) by the use of specific or selective precipitants; (c) by generation of reagents in the homogeneous phase; and (d) by the use of masking and demasking reagents to eliminate interference. These methods are discussed more fully in the following sections.



# **PRECIPITATION BY CHANGE OF HYDROGEN ION CONCENTRATION**

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Precipitation by regulation of the hydrogen ion concentration of a solution is one of the most widely used operations in analytical chemistry. Metal ions are frequently separated by precipitation as the hydroxides, sulfides, phosphates, carbonates, chromates, and oxalates. Since these and many other precipitating ions are anions of weak acids, their concentration in solution is dependent on the hydrogen ion concentration of the solution. Therefore, if there is a sufficient difference in the solubility of two (or more) metal hydroxides, or of any of the above-mentioned salts, important separations can be accomplished by fractional precipitation by a suitable control of the pH of the solution. The problem of fractional precipitation is largely a matter of determining the pH at which the precipitation of a given component (or components) should be carried out, and the proper method for adjusting the solution to, and maintaining at, this pH.

## **PRECIPITATION OF METALS AS THE HYDROXIDES**

The separation of metals by fractional precipitation as their hydroxides is of great importance in analytical chemistry for the following reasons: (1) the solubilities of the metal hydroxides vary widely, ranging from the extremely insoluble hydroxides of iron and titanium to the very soluble potassium hydroxide; (2) the hydrogen ion concentration and, consequently, the hydroxyl ion concentration, of a solution may be adjusted to any value within the wide range from pH <1 to 14. Further, the hydrogen ion concentration of a solution can be adjusted to, and maintained at, a relatively fixed value by the use of suitable buffers over a similar range.

**Precipitation with Ammonium Hydroxide.**—Ammonium hydroxide is one of the most commonly used reagents for the precipitation of metal hydroxides or oxides. The number of metals so precipitated is rather large, and includes the following: aluminum, beryllium, chromium, gallium, indium, iron(III), niobium, the rare earths, tantalum, thallium, thorium, titanium, uranium, and zirconium. In addition, arsenic(V), phosphorus(V), and vanadium(V) are also precipitated as arsenates, phosphates, and vanadates with one or more of the above ions.

Alone, arsenic, chromium(VI), manganese(VII), phosphorus, sulfur, and vanadium(V), are not precipitated in either strongly acidic or strongly basic solution.

Silicon and the higher oxidation states of antimony, lead, manganese, titanium, and tungsten are predominantly acidic in character and consequently their oxides and hydroxides are precipitated from strongly acidic solutions.<sup>1</sup>

Barium, calcium, magnesium, manganese, and strontium are not precipitated by ammonium hydroxide in the presence of ammonium chloride. Cobalt, copper, nickel, and zinc ions precipitate, but redissolve due to the formation of complex amines.

When ammonium hydroxide precipitation is used quantitatively, silicon and metals of the hydrogen sulfide group should be absent, or if present should be removed prior to the hydroxide precipitation. This is necessary even though some of these ions are almost completely precipitated by ammonium hydroxide.

Ammonium hydroxide is not generally satisfactory if much zinc is present, particularly in the presence of chromium. Results are also usually unsatisfactory if cobalt or copper is present. Boron interferes, and should be removed.

The method used in precipitating with ammonium hydroxide depends on the ions present. Thus, for the precipitation of aluminum, and of phosphorus in the presence of aluminum or iron, the pH of the solution must be adjusted very care-

TABLE 5-1. APPROXIMATE pH OF PRECIPITATION OF HYDROXIDES AND OXIDES <sup>2</sup>

Element	pH	Reagents
Nb, Si, Ta, W	<1	Conc. HCl, HNO <sub>3</sub> , HClO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub>
Sb(V), Sn(IV)	<1	Conc. HNO <sub>3</sub> , HClO <sub>4</sub>
Mn(IV)	<1	Conc. HNO <sub>3</sub> or HClO <sub>4</sub> with KClO <sub>3</sub>
Pb(IV)	<1	Conc. HNO <sub>3</sub>
Os(IV)	1-2	
Ce(IV), Sb(III), Ti, Zr	2-3	
Fe(III), Hg(I), Hg(NO <sub>3</sub> ) <sub>2</sub> , Sn(II), Th	3-4	pH 3-5: Acetic acid—Acetate Benzoic acid—Benzoate
U(VI)	4-5	
Al, Be, Cr(III), Ir(IV)	5-6	
Cu, Fe(II), Nd, Pb, Pd, Rh, Ru, Sm, Y, Yb	6-7	pH 6-8: BaCO <sub>3</sub> , CaCO <sub>3</sub> , CdCO <sub>3</sub> HgO, ZnO
Cd, Ce(III), Co, La, Ni, Pr, Zn	7-8	
HgCl <sub>2</sub> , Mn(II), Ag	8-9	pH 8-10: NH <sub>4</sub> OH—NH <sub>4</sub> Cl (except Ag) MgO(pH 9.5)
Mg	11	NaOH
Ba, Ca, Sr	>12	NaOH (Incomplete)

<sup>1</sup> Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., Applied Organic Analysis, 2nd Ed., John Wiley and Sons, New York, 1953.

<sup>2</sup> Most of these values are taken from the work of Britton, H. T. S., J. Chem. Soc., 125, 2124, 1927, and Hydrogen Ions, Chapman and Hall, London, 1932. Values for the platinum metals are given by Bowles, J. A. C., and Partridge, H. M., Ind. Eng. Chem., Anal. Ed., 9, 124, 1937, and by R. Gilchrist at the National Bureau of Standards.

fully, since only a slight excess of ammonium hydroxide is permissible. This is also probably true for beryllium, gallium, and scandium. On the other hand, careful neutralization is not similarly necessary for elements such as iron, titanium, and zirconium, which are quantitatively precipitated at lower pH.<sup>1</sup>

The pH at which precipitation of a metal hydroxide begins is fairly definite, but depends somewhat on the concentration of the metal ion. For example, zinc hydroxide begins to precipitate at pH 5.80 from a 0.25 M zinc sulfate solution, at pH 6.17 from a 0.05 M solution, and pH 6.5 from a 0.01 M solution.<sup>2</sup> The pH at which precipitation begins also depends on the kind of anions present. Thus, lanthanum(III) hydroxide begins precipitation at pH 7.61 from a sulfate solution and at pH 8.03 from a chloride solution.<sup>4</sup>

Further, for most hydroxides there is a range of 1.5 to 2 pH units from the beginning of precipitation until precipitation is complete. Thus, if the metals are arranged in the order of pH of precipitation, there is an overlap of the range of completeness of precipitation. This is shown in Table 5.1, which gives the approximate pH for the precipitation of the hydroxides of the various metals.

Despite the overlap of precipitation range, however, as a general rule metals for which pH values for the beginning of precipitation differ by as much as 3 pH units, should be separated by fractional precipitation of their hydroxides unless the relative concentrations of the ions is not favorable. Thus, by a proper control of pH, aluminum, chromium(III), and iron(III) can be separated from barium, calcium, cobalt, manganese, nickel, strontium, and zinc. Iron(III) is easily separated at pH 3, although separations of aluminum and chromium are more difficult, since for most conditions of pH these metals are not quantitatively separated without precipitation of some other metals.

The proper pH for the separation of one element from another is the lower of the two pH values for the precipitation of the two components. The amphoteric elements, such as aluminum, chromium(III), tin(II), and zinc are exceptions to this rule. The hydroxides of these metals dissolve in an excess of a strong base. Separations based on amphoterism, however, are not extensively used in quantitative analysis, because resolution is not usually complete.<sup>5</sup>

It should be noted that for several reasons there are objections to quantitative separations based on the precipitation of hydroxides with ammonium hydroxide. The precipitates of the hydrous oxides are gelatinous, and consequently difficult to filter and wash. Further, they have a strong tendency to absorb both anions and cations from the solution and thus produce an impure precipitate. Despite these practical objections, however, the method is capable of yielding very satisfactory results for a number of important applications.

*Precipitations with Suspensions of Slightly Soluble Oxides and Carbonates.*—Satisfactory methods have been developed for precipitating the polyvalent metals by adjusting the pH of the medium with slightly soluble oxides and carbonates. These substances exert a buffer action when the corresponding metal ion is present in the solution. Oxides and carbonates for which procedures have been described are as follows:

(1) Barium Carbonate.—This compound has been used for the separation of aluminum, chromium, iron(III), titanium, uranium, and zirconium (also phos-

<sup>2</sup> Kolthoff, I. M., and Kameda, T., J. Am. Chem. Soc., 53, 832, 1931.

<sup>4</sup> Kolthoff, I. M., and Sandell, E. B., Textbook of Quantitative Inorganic Analysis, Macmillan, New York, 1943.

<sup>5</sup> Ayres, G. H., Quantitative Chemical Analysis, Harper and Bros., New York, 1958.

phorus and vanadium in the presence of the preceding metals) from cobalt, iron, manganese, nickel, and zinc. Zinc and manganese are more completely separated than cobalt and nickel. Beryllium is completely precipitated from a hot solution, but only incompletely from a cold solution. Metals of the cerium group are precipitated from a hot solution. They are also precipitated from a cold solution, though some slowly. Yttrium group metals are precipitated only incompletely, and also slowly.

(2) **Cadmium Carbonate.**—Cadmium carbonate gives a solution of pH 6.5, and has been used for the separation of chromium and vanadium from iron(II). Sulfate does not interfere.<sup>6</sup>

(3) **Calcium Carbonate.**—Calcium carbonate gives a pH of 7.4. It is less satisfactory than barium carbonate for separations.

(4) **Lead Carbonate.**—Lead carbonate gives a solution of pH 6.2, and precipitates completely cerium(IV), iron(III), thorium, and zirconium. The following are not precipitated: cerium(III), lanthanum, neodymium, praseodymium, samarium, yttrium, and the yttrium group metals. Aluminum, chromium(III), and uranium are only incompletely precipitated.<sup>7</sup>

(5) **Magnesium Oxide.**—Magnesium oxide gives a pH of 10.5, and is used when a strongly basic solution is required.

(6) **Mercuric Oxide.**—Mercuric oxide gives a pH of 7.4, and is best used as a precipitant for solutions containing the chlorides of the metals. Aluminum, chromium, and iron are completely precipitated from a cold solution, but the precipitate usually contains barium, calcium, and strontium if these ions are present. Beryllium, cerium(III), cobalt, lanthanum, nickel, and zinc are incompletely precipitated from both cold and hot solutions, but are more completely precipitated from hot solutions. Manganese is precipitated slowly or not at all from cold solutions.<sup>8</sup>

(7) **Zinc Oxide.**—Zinc oxide gives a pH of 5.5, and is useful for precipitation from solutions containing sulfuric acid or sulfates. In the presence of large amounts of iron(III), zinc oxide precipitates completely aluminum, arsenic, chromium, iron, phosphorus, tin, titanium, uranium, vanadium, tungsten, and zirconium, and almost all copper, molybdenum, and silicon. Very little cobalt or manganese is precipitated, and a second precipitation gives a complete separation of cobalt and manganese from the above-mentioned elements. Separation of nickel is not entirely satisfactory.<sup>9</sup>

**Precipitation with Weak Organic Bases.**—A number of weak organic bases have been used as satisfactory precipitants for certain of the metal hydroxides. These are:

(1) **Phenylhydrazine.**—This compound precipitates quantitatively thorium, titanium, and zirconium (and also aluminum under certain conditions) from dilute, slightly acidic solutions of salts of these metals. Phosphorus and vanadium are also precipitated completely if not in excess of the other metals present. Cerium, iron(III), and uranium are reduced and precipitated only incompletely, if at all.

Cadmium, cobalt, mercury, nickel and zinc, when present in sufficient concentration, may form slightly soluble addition products with the reagent. Calcium, iron(II), magnesium, manganese, and strontium are not precipitated. Some impor-

<sup>6</sup> Cain, J. R., J. Ind. Eng. Chem., 3, 478, 1911.

<sup>7</sup> Giles, W. B., Chem. News, 92, 1, 30, 1905.

<sup>8</sup> Smith, E. F., and Heyl, P. R., Z. anorg. Chem., 7, 82, 1892.

<sup>9</sup> Hoffman, J. I., Bur. Standards J. Research, 7, 883, 1931.

tant separations which have been recommended are: (a) titanium and zirconium from iron; titanium, thorium, and zirconium from beryllium; and aluminum from iron;<sup>10</sup> and (b) aluminum from calcium, iron, magnesium, and manganese.<sup>11</sup>

(2) **Aniline.**—Aniline precipitates quantitatively aluminum, cerium, chromium, iron(III), thorium, titanium, and zirconium. Calcium, iron(II), magnesium, manganese, and strontium are not precipitated.<sup>10</sup> Aniline has been used to separate thorium from lanthanum and praseodymium, and also zirconium from lanthanum,<sup>12</sup> and chromium from manganese.<sup>13</sup>

(3) **Quinoline.**—This reagent precipitates quantitatively the hydroxides of cerium, lanthanum, neodymium, praseodymium, thorium, and zirconium.<sup>12</sup>

(4) **Hexamethylenetetramine.**—This weak base precipitates hydroxides of aluminum, chromium, iron(III), and zinc when boiled with aqueous solutions of their salts.<sup>14</sup> Titanium, uranium, and zirconium are also precipitated from solutions containing ammonium chloride.<sup>15</sup> This reagent has been used to separate aluminum and iron from the alkali metals, calcium, cobalt, manganese, nickel, and zinc.<sup>16</sup>

(5) **Pyridine.**—Pyridine precipitates quantitatively aluminum, chromium, iron, titanium, uranium, and zirconium.<sup>17</sup> This reagent has been used to separate aluminum, chromium, and iron from cobalt, manganese, and nickel.

**Precipitation with Buffer Solutions.**—Various buffers have been used to control the pH of a solution so as to effect practical separations of metals by precipitation. The most important of these are:

(1) **The Basic Acetate Method.**—Although the basic acetate method has largely been replaced by ammonium hydroxide precipitation, it may still be used to advantage in a number of important separations. In this method the pH of the medium is adjusted by an acetic acid-sodium acetate or acetic acid-ammonium acetate buffer. It is principally used to separate iron(III) from cobalt, copper, or zinc; or iron(III) from nickel when either is present in large amount; or large amounts of iron(III) from manganese. An important advantage of such separations is that there is little local lowering of pH during precipitation, and consequently little coprecipitation of the divalent metals.

The basic acetate method is not satisfactory for aluminum, since zinc and other metals are partially precipitated. Two precipitations, however, give good separations. This method cannot be used for chromium, uranium, and some of the rare earth metals, although precipitation of cerium(IV), thorium, and zirconium is apparently complete from a boiling solution. Phosphorus is also precipitated if not in excess of other metals which form insoluble phosphates. Phosphorus can be removed by first adding a known weight of pure iron(III) chloride as a preliminary to the determination of the alkaline earth metals and magnesium in the analysis of some phosphates.<sup>18</sup>

(2) **Sodium Succinate.**—This reagent has been used to separate aluminum and iron from cobalt, manganese, nickel, and zinc. It is equally as useful as the basic

<sup>10</sup> Allen, E. T., *J. Am. Chem. Soc.*, 25, 421, 1903.

<sup>11</sup> Hess, W. H., and Campbell, E. D., *J. Am. Chem. Soc.*, 21, 776, 1899.

<sup>12</sup> Jefferson, A. M., *J. Am. Chem. Soc.*, 24, 540, 1902.

<sup>13</sup> Schoeller, W. R., and Schraube, W., *Chem.-Ztg.*, 33, 1237, 1909.

<sup>14</sup> Lehman, L., and Kabat, E. A., *J. Chem. Ed.*, 11, 374, 1934.

<sup>15</sup> Ray, P., *Z. anal. Chem.*, 86, 13, 1931.

<sup>16</sup> Ismail, A. M., and Harwood, H. F., *Analyst*, 62, 185, 1937. Also, Akiyama, T., *J. Pharm. Soc. Japan*, 56, 893, 1936; 57, 19, 1937.

<sup>17</sup> Ostroumov, E. A., *Z. anal. Chem.*, 106, 170, 244, 1936, and *Zavodskaya Lab.*, 6, 16, 1937.

<sup>18</sup> Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd Ed., John Wiley and Sons, New York, 1953.

acetate method for separating iron and aluminum from nickel, but is less so for separating iron from cobalt, manganese, and zinc. Less care is required in adjusting the pH than with the basic acetate method, and aluminum is more completely precipitated. This buffer does not always give satisfactory results.

(3) **Benzoic Acid-Ammonium Benzoate.**—This buffer gives excellent results for the precipitation of aluminum, chromium, and iron, which is quantitative at pH 3.8. Not any of the divalent metals precipitate under proper conditions, and coprecipitation is very slight when correct procedures are employed.<sup>19</sup>

(4) **Formic Acid-Sodium Formate.**—Since formic acid has an ionization constant approximately ten times that of acetic acid, a formic acid-sodium formate buffer can be used when precipitation is to be carried out at a lower pH than for the basic acetate method. This system, however, does not in all cases give satisfactory results.<sup>20</sup>

(5) **Salicylic Acid-Ammonium Salicylate.**—This buffer has been used for the separation of niobium, tantalum, thorium, and zirconium from aluminum and titanium.<sup>21</sup> A fair separation of niobium and tantalum from titanium is achieved by repeated precipitation with salicylic acid.<sup>22</sup>

**Precipitation with Reagents That React with the Hydrogen Ion.**—A useful method for adjusting the pH of a solution consists of adding a reagent, or a mixture of reagents, which react with the hydrogen ion. For example, if a solution of an aluminum salt is boiled with sodium or ammonium nitrite, the hydrogen ion formed by the hydrolysis of the aluminum salt combines with the nitrite ion to form nitrous acid, which decomposes with the formation of water and the evolution of the oxides of nitrogen.<sup>23</sup> Iron and chromium are also precipitated in this manner. Other reagents which have been used for a similar purpose are potassium cyanate,<sup>24</sup> sodium thiosulfate,<sup>25</sup> and mixtures of potassium iodide and potassium iodate or potassium bromide and potassium bromate.<sup>26</sup> The latter reagents have been used for separating such elements as aluminum, chromium, iron, cobalt, nickel, and tin,<sup>27</sup> and bismuth from cadmium, copper, lead, and zinc.<sup>28</sup> Sodium hyposulfite,  $\text{Na}_2\text{S}_2\text{O}_4$ , has been used to reduce iron and precipitate aluminum and beryllium.<sup>29</sup>

When urea is boiled with a weakly acidic solution it hydrolyzes slowly to form ammonia, which causes a gradual increase in the pH of the solution. This is one of the better reagents used for the precipitation of the hydrous oxides of the polyvalent metals.

The reagents included in this section are used for the precipitation from homogeneous solutions, which is discussed more fully on page 139.

**Precipitation with Sodium Hydroxide.**—Sodium hydroxide is not so frequently used for hydroxide precipitation as ammonium hydroxide. It has been used, however, to separate chromium, iron, titanium, the rare earths, and zirconium from

<sup>19</sup> Kolthoff, I. M., Stenger, V. A., and Moskovitz, B., *J. Am. Chem. Soc.*, **56**, 812, 1934.

<sup>20</sup> Funk, W., *Z. anal. Chem.*, **45**, 503, 1906.

<sup>21</sup> Dittrich, M., and Freund, S., *Z. anorg. Chem.*, **56**, 344, 1907.

<sup>22</sup> Müller, J. H., *J. Am. Chem. Soc.*, **33**, 1506, 1911; Schoeller, W. R., and Deering, E. C., *Analyst*, **52**, 625, 1927.

<sup>23</sup> Schirm, E., *Chem. Ztg.*, **33**, 877, 1237, 1909; **35**, 980, 1911.

<sup>24</sup> Ripan, R., *Bull. Soc. Stiinte Cluj*, **3**, 311, 1927; **4**, 28, 1928.

<sup>25</sup> Clennel, J. E., *Metal Ind.*, **21**, 273, 1922.

<sup>26</sup> Glassman, B., *Ber.*, **39**, 3368, 1906; Moody, E., *Z. anal. Chem.*, **46**, 247, 1907; Stock, A., *Ber.*, **33**, 548, 1900; Stock, A., and Massaciu, C., *Ber.*, **34**, 467, 1901.

<sup>27</sup> Moody, S. E., *Am. J. Sci.*, **20**, 181, 1905.

<sup>28</sup> Moser, L., and Maxymowicz, W., *Z. anal. Chem.*, **67**, 248, 1925–26.

<sup>29</sup> Barbier, P., *Bull. Soc. Chem.*, [4], **7**, 1027, 1910.

aluminum, phosphorus, and vanadium. Titanium is not completely precipitated unless iron is present. The alkaline earths are also precipitated if carbonate is present. Aluminum separations are not complete if magnesium or nickel is present. Uranium is incompletely precipitated if vanadium or carbonate is present.

If an oxidizing agent, such as sodium or hydrogen peroxide, is used in conjunction with sodium hydroxide, chromium, uranium, and vanadium are not precipitated. If uranium is present, sodium carbonate should also be used. Cobalt(III) and nickel(III) hydroxides are precipitated by the use of bromine or other oxidizing agents with sodium hydroxide.

## PRECIPITATION OF METALS AS OXIDES FROM SOLUTIONS OF STRONG ACIDS

The oxides of the acidic elements, antimony, lead, niobium, silicon, tantalum, tin, and tungsten, in their highest oxidation state, and manganese(IV), are precipitated from solutions of strong acids. Tungsten(VI), tantalum(V), niobium(V), and silicon(IV) are precipitated by means of concentrated hydrochloric acid, nitric acid, sulfuric acid, and perchloric acid. Antimony(V) and tin(IV) are precipitated by means of concentrated nitric or perchloric acid, but not by hydrochloric acid. Manganese dioxide is precipitated by concentrated nitric or perchloric acid with potassium chlorate, and lead dioxide with concentrated nitric acid.

## PRECIPITATION OF METALS AS SULFIDES

The precipitation of metals as sulfides is based on the same theoretical principle as that of the hydroxides. There is an enormous difference in the solubilities of the metal sulfides, ranging from the very soluble potassium and sodium sulfides to the very insoluble sulfides of mercury(II) and arsenic ( $K_s \sim 10^{-53}$ ). Further, as with the hydroxyl ion concentration, the sulfide ion concentration can be varied from approximately 1 *M* in sodium sulfide solution to  $10^{-22}$  *M* in a dilute hydrochloric acid solution of hydrogen sulfide. Since the sulfide ion concentration is related to the hydrogen ion concentrations as

$$[H^+]^2 \times [S^{2-}] = 1.1 \times 10^{-23}$$

it is apparent that many valuable separations can be accomplished by precipitations with hydrogen sulfide in solutions of different pH.

The elements precipitated by hydrogen sulfide may be grouped into four classes depending on the pH of the solution from which precipitation is made. These are: (1) strong acid of pH < 1; (2) dilute acid of pH 2-3; (3) very slightly acidic solution of pH 5-6; and (4) basic solution of pH > 7.<sup>30</sup>

(1) *Strong Acid Solution of pH < 1*.—Elements of this group are precipitated from solutions ranging from 0.25 to 13 *M* in hydrochloric acid. These elements are divided into two groups as follows: (a) *the Copper Subgroup*, which consists of bismuth, cadmium, copper, lead, mercury, osmium, palladium, rhodium, ruthenium, and silver; gallium, indium, and thallium are partially or completely precipitated in the presence of certain members of this group; and (b) *the Arsenic Subgroup*, which consists of antimony, arsenic, germanium, gold, iridium, molyb-

<sup>30</sup> Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd Ed., John Wiley and Sons, New York, 1953.

denum, platinum, selenium, tellurium, and tin. Tungsten and vanadium are also precipitated partially or completely with certain elements of this group in the absence of tartaric acid.

Precipitates of sulfides of this group are often contaminated with elements of other groups due to the formation of mixed sulfides. Zinc, for example, is precipitated with cadmium, copper, and mercury; thallium with antimony, arsenic, and copper; and cobalt and nickel with tin(IV).

There are few useful separations within this group based on hydrogen ion control. The order of increasing solubility of the sulfides is approximately: arsenic(V), arsenic(III), molybdenum(VI), mercury(II), copper, antimony, bismuth, tin(IV), cadmium, lead, tin(II).

The most important separation is based on the fact that of this group only arsenic(V) is precipitated from cold 10 *N* hydrochloric acid. This yields a satisfactory method for the separation of arsenic from antimony and tin, but it fails with copper, germanium, mercury, and molybdenum, which also form slightly soluble sulfides.

Precipitation of sulfides of this group is usually carried out from hydrochloric acid solution, although molybdenum and platinum are more easily precipitated from sulfuric acid.

(2) *Dilute Acid Solution*.—In the absence of members of the preceding group, and also elements which hydrolyze at a pH of 2–3, a number of elements may be precipitated with hydrogen sulfide from a 0.01 *N* sulfuric acid solution. Separation from the members of the next group is not sharp, and for accurate results, reprecipitation must be carried out. The element most successfully precipitated in this group is zinc, and this results primarily from the fact that gallium, indium, and thallium, which usually cause difficulty, are not often present. A proper pH for precipitation within this group is given by a 0.01 *N* solution of sulfuric acid. Precipitation of zinc sulfide from a formic acid solution containing ammonium citrate and formate gives good results.

(3) *Slightly Acidic Solution of pH 5–6*.—The separations of cobalt and nickel from manganese in the absence of iron are the only useful separations within this group. Indium and thallium are completely precipitated, and iron partially precipitated if much acetic acid is present. Gallium is also partially precipitated in the presence of certain other elements.

The proper pH for precipitation of elements of this group is usually obtained by use of an acetic acid-ammonium or sodium acetate buffer. Since precipitation is rarely complete in this group, special provision is necessary to recover cobalt and nickel from the filtrate.

(4) *Basic Solution*.—Most elements are precipitated as sulfides from a basic solution. Ordinarily, precipitation of this group follows the separation of the elements precipitated from acidic solutions, and also is carried out in conjunction with complexing agents, such as tartrate. The latter eliminates interference by such elements as aluminum, chromium, the rare earths, titanium, and uranium. Following such treatment the metals precipitated are usually iron and manganese, and also elements of other groups, such as cobalt, nickel, and zinc.

## PRECIPITATION WITH ORGANIC REAGENTS

With organic precipitants, as with inorganic reagents, considerable selectivity can be achieved by carrying out precipitation under controlled conditions of acidity. Although organic reagents are far too numerous to consider this effect in de-



tail, the influence of pH on the completeness of precipitation of various cations by means of 8-hydroxyquinoline will illustrate this general principle. The pH range for the complete precipitation of a number of cations is given in Table 5-2. Clearly, a number of important separations are indicated, as for example aluminum, iron, and zinc from calcium, magnesium, and lead. Coprecipitation causes difficulties, however, and a careful control of conditions is necessary.

TABLE 5-2. PRECIPITATION OF METALS BY 8-HYDROXYQUINOLINE

Metal	pH Range for Complete Precipitation	Reference <sup>21</sup>
Indium	2.5-3.0	b
Vanadium	2.7-6.1	c
Iron(III)	2.8-11.2	c
Gallium	> 3.1	f
Molybdenum	3.3-7.6	c
Thallium(III)	4.0-8.0	f
Uranium	4.07-8.84	c
Cobalt	4.33-14.5	a
Aluminum	4.39-9.80	c
Thorium	4.43-8.80	c
Nickel	4.57-9.97	c
Zinc	4.58-13.4	a
Bismuth	4.8-9.4	c
Tungsten	4.95-5.65	a
Plutonium(VI)	5	d
Copper	5.33-14.55	a
Cadmium	5.66-14.58	a
Manganese	5.87-9.51	c
Antimony	6	g
Scandium	6.5-8.5	h
Lanthanum	> 7	e
Lead	8.44-12.28	c
Cerium(III)	> 9.4	e
Magnesium	9.44-12.66	a
Calcium	9.5-10	i

<sup>21</sup> Letters refer to the following publications.

- a—Fleck, H. R., and Ward, A. M., *Analyst*, **58**, 388, 1933; **62**, 378, 1937.
- b—Geilmann, W., and Wrigge, Fr. W., *Z. anorg. Chem.*, **209**, 129, 1932.
- c—Goto, H., *J. Chem. Soc., Japan*, **54**, 725, 1933; **56**, 314, 1935; *Sci. Repts. Tohoku Imp. Univ.*, **26**, 391, 1937; **26**, 418, 1938.
- d—Harvey, G. B., *et al.*, *J. Chem. Soc.*, **1947**, 1010.
- e—Misumi, S., *J. Chem. Soc., Japan, Pure Chem. Sect.*, **73**, 931, 1952.
- f—Moeller, T., and Cohen, A. J., *Anal. Chem.*, **22**, 686, 1950.
- g—Pirtea, Th., *Z. anal. Chem.*, **118**, 26, 1939-40.
- h—Pokras, L., and Bernays, P. M., *J. Am. Chem. Soc.*, **73**, 7, 1951.
- i—Rynasiewicz, J., and Polley, M. E., *Anal. Chem.*, **21**, 1398, 1949.

# ***SPECIFIC AND SELECTIVE PRECIPITANTS***

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## **ORGANIC PRECIPITANTS**

For many years one of the principal objectives of the analytical chemist has been the discovery of a specific reagent for each element. With such reagents it would then be possible to determine each element in the presence of any other element without interference. Not any of the classical inorganic reagents are specific in their reactions, and accordingly the analytical chemist has turned to the investigation of the analytical characteristics of organic compounds in an effort to discover specific reagents. A very extensive search for such compounds has been carried out over a long period of time, and it now appears likely that, although some reagents approach the ideal of specificity, a complete set of specific reagents will never be fully realized. For the most part organic compounds react with a group of elements, and in some cases a fairly small group, and for this reason they are generally regarded as group reagents, or are in other words selective in their action.

The usefulness of selective reagents can often be improved by utilizing various methods for reducing the number of elements with which they react. These methods include a careful control of the hydrogen ion concentration of the solution (page 92), and the use of masking agents that form stable complexes with elements that might otherwise interfere with a given determination. For a discussion of common masking agents in precipitation reactions, see page 150.

There are many important advantages in the use of organic reagents over inorganic reagents when used as precipitants for inorganic substances. Among these are the following: (a) it is often possible to attain a degree of selectivity not possible with an inorganic reagent; (b) many organic reagents are acidic and therefore improved selectivity in precipitation reactions can be achieved by a careful control of the hydrogen ion concentration; (c) the precipitates formed in reactions of organic reagents with inorganic ions are often extremely insoluble, and frequently, too, are of very high molecular weight. They are accordingly well adapted to micro and semimicro procedures.

There are also certain disadvantages attending the use of organic reagents. Among the more common of these are: (a) organic compounds are frequently of such low water solubility that their use is restricted, either because of the difficulty of preparing reagent solutions, or because of possible contamination of precipitates which they form; (b) many organic compounds are so unstable that serious inconveniences result from their use and storage; (c) organic compounds are

often expensive or difficult to obtain; (d) the presence of organic constituents in precipitates is sometimes a serious disadvantage in inorganic analysis.

In general, however, the advantages far outweigh the disadvantages, and the use of organic reagents for inorganic analysis has developed into an extremely important part of analytical chemistry.

In this section we are concerned with the organic compounds which are commonly used as precipitants for inorganic anions and cations. The compounds included in this group are substances that differ widely in their constitution and in the nature of their reactions, but that possess the common characteristic of forming insoluble compounds with inorganic ions under certain well-defined conditions. Some of these reagents form normal ionic salts, while others form insoluble chelate compounds. Still others combine with inorganic substances in a manner not fully understood, as perhaps through a process involving adsorption. Tannin is typical of this group. Still others do not combine directly with the inorganic substance, but react with the medium or with one another to yield products capable of causing the precipitation of these substances. Such reagents are particularly significant in the precipitation of substances in the homogeneous phase. Thus, thioacetamide reacts with water to form hydrogen sulfide, which forms precipitates with many metal ions.

The precipitants described in the following sections are those which are most frequently used in quantitative inorganic analysis. Although fairly extensive, this group comprises only a very small fraction of those reagents reported in a very extensive literature. For other reagents, or for more detailed information on those included here, the analyst should consult one of the many available reference works available on this subject.<sup>32</sup>

The organic compounds most frequently used for precipitation of the metals and anions are given in Table 5-3.

TABLE 5-3. ORGANIC PRECIPITANTS

<i>The Metals</i>	
Aluminum	Benzoic acid
	N-Benzoylphenylhydroxylamine
	Cupferron
	5,7-Dibromo-8-hydroxyquinoline
	8-Hydroxyquinoline
	Succinic acid
Ammonium	Tetraphenylboron

<sup>32</sup> Belcher, R., and Wilson, C. L., *New Methods in Analytical Chemistry*, Reinhold, New York, 1955; Busev, A. I., and Polianskii, N. G., *The Use of Organic Reagents in Inorganic Analysis*, Pergamon Press, London, 1960; Duval, C., *Inorganic Thermogravimetric Analysis*, Elsevier, Amsterdam, 1953; Feigl, F., *Chemistry of Specific, Selective and Sensitive Reactions*, Academic Press, New York, 1949; Flagg, J. F., *Organic Reagents, Interscience*, New York, 1948; Johnson, W. C., *Organic Reagents for Metals*, Chemical Publishing Co., New York, 1955; Mellan, I., *Organic Reagents in Inorganic Analysis*, Blackiston, Philadelphia, 1941; Prodingen, W., *Organische Fällungsmittel in der quantitativen Analyse*, Ferdinand Enke, Stuttgart, 1957; Welcher, F. J., *Organic Analytical Reagents*, 4 vols., Van Nostrand, New York, 1947-48; Yoc, J. H., and Sarver, L. A., *Organic Analytical Reagents*, John Wiley and Sons, Inc., New York, 1941.

TABLE 5-3. (Continued)

*The Metals*

Antimony	Bismuthiol(II)
	Gallic acid
	8-Hydroxyquinoline
	Phenylthiohydantoic acid
	Pyrogallol
	Tannic acid
Arsenic	Bismuthiol(II)
Beryllium	Benzoic acid
	Cupferron
	8-Hydroxyquinoline
	Tannin
Barium	Oxalic acid
Bismuth	Benzoic acid
	Bismuthiol(II)
	Cupferron
	8-Hydroxyquinoline
	Mercaptobenzothiazole
	Phenylarsonic acid
	Pyrogallol
	Salicylaldehyde
Cadmium	Thionalide
	Anthranilic acid
	Ethylenediamine
	2-(o-Hydroxyphenyl)benzoxazole
	8-Hydroxyquinoline
	Mercaptobenzothiazole
	$\beta$ -Naphthoquinoline
	Oxalic acid
	Phenylthiohydantoic acid
	Phenyltrimethylammonium iodide
	Propylenediamine
	Pyridine (+ SCN <sup>-</sup> )
	Quinaldinic acid
	Quinoline-8-carboxylic acid
	Tetraphenylarsonium chloride
Calcium	Chloranilic acid
	Oxalic acid
	Picolonic acid
Cerium	8-Hydroxyquinoline
	Oxalic acid

TABLE 5-3. (Continued)

<i>The Metals</i>	
Cesium	Dipicrylamine Tetraphenylboron
Chromium	8-Hydroxyquinoline
Cobalt	Anthranilic acid 8-Hydroxyquinoline 1-Nitroso-2-naphthol Oxalic acid Phenylthiohydantoic acid Pyridine (+ SCN <sup>-</sup> )
Copper	Alizarin blue Anthranilic acid $\alpha$ -Benzoinoxime Benzotriazole N-Benzoylphenylhydroxylamine Cupferron 5,7-Dibromo-8-hydroxyquinoline Ethylenediamine (+ HgI <sub>4</sub> <sup>-</sup> ) 8-Hydroxyquinoline Mercaptobenzothiazole Neocupferron 1-Nitroso-2-naphthol Phenylthiohydantoic acid Propylenediamine Pyridine (+ SCN <sup>-</sup> ) Quinaldinic acid Quinoline-8-carboxylic acid Salicylaldoxime Tetraphenylboron Thionalide o-(p-Toluylsulfonamide)aniline
Gallium	Cupferron 5,7-Dibromo-8-hydroxyquinoline 8-Hydroxyquinoline Tannin
Germanium	8-Hydroxyquinoline $\beta$ -Naphthoquinoline Tannin
Gold	Dimethylglyoxime Hydroquinone Mercaptobenzothiazole Quinoline-8-carboxylic acid

TABLE 5-3. (Continued)

*The Metals*

Gold	Resorcinol Thiophenol
Indium	Diethyldithiocarbamate 8-Hydroxyquinoline
Iridium	Mercaptobenzothiazole
Iron	Acetic acid Benzoic acid N-Benzoylphenylhydroxylamine p-Butylphenylarsonic acid m-Cresoxyacetic acid Cupferron 5,7-Dibromo-8-hydroxyquinoline 8-Hydroxyquinoline Neocupferron 1-Nitroso-2-naphthol Succinic acid
Lanthanum	8-Hydroxyquinoline Oxalic acid
Lead	Anthranilic acid 8-Hydroxyquinoline Mercaptobenzothiazole Phenylthiohydantoic acid Phthalic acid Picrolonic acid Salicylaldoxime Thionalide
Magnesium	8-Hydroxyquinoline 8-Hydroxyquinaldine Oxalic acid
Manganese	Anthranilic acid 8-Hydroxyquinoline Oxalic acid Picrolonic acid Pyridine (+ $\text{SCN}^-$ ) Tetraphenylarsonium chloride
Mercury	Anthranilic acid Cupferron Ethylenediamine 2-(o-Hydroxyphenyl)benzimidazole Phenylthiohydantoic acid

TABLE 5-3. (Continued)

*The Metals*

Mercury	Propylenediamine Tetraphenylarsonium chloride Thionalide
Molybdenum	$\alpha$ -Benzoinoxime Cinchonine 8-Hydroxyquinoline
Nickel	Anthranilic acid $\alpha$ -Benzildioxime Cycloheptanedionedioxime Cyclohexanedionedioxime Dicyandiamidine Dimethylglyoxime $\alpha$ -Furildioxime 8-Hydroxyquinoline Oxalic acid Pyridine (+ $\text{SCN}^-$ ) Salicylaldoxime
Niobium	N-Benzoylphenylhydroxylamine Cupferron 8-Hydroxyquinoline Phenylarsonic acid Tannin
Osmium	Benzotriazole
Palladium	p-Aminoacetophenone $\alpha$ -Benzildioxime Cycloheptanedionedioxime Cyclohexanedionedioxime Dimethylglyoxime $\beta$ -Furaldoxime m-Nitrobenzoic acid 1-Nitroso-2-naphthol Quinaldinic acid Salicylaldoxime
Platinum	Formic acid
Plutonium	Benzoic acid Mandelic acid m-Nitrobenzoic acid Phenylarsonic acid Picrolonic acid

TABLE 5-3. (Continued)

<i>The Metals</i>	
Potassium	Dipicrylamine Tetraphenylboron
Rhenium	Nitron Tetraphenylarsonium chloride
Rubidium	Dipicrylamine Tetraphenylboron
Scandium	Oxalate
Silver	Ethylenediamine (+ I <sup>-</sup> ) Hydroquinone Propylenediamine (+ I <sup>-</sup> ) Quinoline-8-carboxylic acid Thionalide
Sodium	Acetic acid
Strontium	Oxalic acid
Tantalum	N-Benzoylphenylhydroxylamine Cupferron Phenylarsonic acid Tannin
Thallium	8-Hydroxyquinoline Mercaptobenzothiazole Tetraphenylarsonium chloride Thionalide
Thorium	N-Benzoylphenylhydroxylamine m-Cresoxyacetic acid Cupferron 8-Hydroxyquinoline m-Nitrobenzoic acid Oxalic acid Phenylarsonic acid Picrolonic acid Quinaldinic acid Sebacic acid Sodium naphthionate Tannin
Tin	N-Benzoylphenylhydroxylamine m-Cresoxyacetic acid Cupferron Phenylarsonic acid Tannin Tetraphenylarsonium chloride



TABLE 5-3. (Continued)

<i>The Metals</i>	
Titanium	N-Benzoylphenylhydroxylamine m-Cresoxyacetic acid Cupferron 5,7-Dibromo-8-hydroxyquinoline p-Hydroxyphenylarsonic acid 8-Hydroxyquinoline Tannin + antipyrine
Tungsten	Benzidine $\alpha$ -Benzoinoxime Cinchonine 8-Hydroxyquinoline Nitron Tannin + antipyrine
Uranium	Benzoic acid Cupferron Ethylenediamine 8-Hydroxyquinoline Quinaldinic acid Tannin
Vanadium	N-Benzoylphenylhydroxylamine Cupferron 8-Hydroxyquinoline
Zinc	Anthranilic acid 8-Hydroxyquinaldine 8-Hydroxyquinoline $\beta$ -Naphthoquinoline Oxalic acid Picrolonic acid Pyridine (+ SCN <sup>-</sup> ) Quinaldinic acid Salicylaldoxime Tetraphenylarsonium chloride
Zirconium	N-Benzoylphenylhydroxylamine p-Bromomandelic acid p-Chloromandelic acid m-Cresoxyacetic acid Cupferron p-Hydroxyphenylarsonic acid 8-Hydroxyquinoline Mandelic acid m-Nitrobenzoic acid Phthalic acid

TABLE 5-3. (Continued)

<i>The Metals</i>	
Zirconium	Phenylarsonic acid n-Propylarsonic acid Quinaldinic acid Tannic acid
<i>The Anions</i>	
Ferricyanide	Benzidine
Ferrocyanide	Benzidine
Fluoborate	Nitron
Fluoride	Triphenyltin chloride
Molybdate	See Molybdenum
Nitrate	Nitron
Perchlorate	Nitron
Periodate	Tetraphenylarsonium chloride
Permanganate	See Manganese
Perrhenate	See Rhenium
Sulfate	Benzidine 4-Chloro-4'-aminodiphenyl 4,4'-Diaminodiphenyl
Tungstate	See Tungsten
Vanadate	See Vanadium

### ANALYTICAL CHARACTERISTICS OF MAJOR ORGANIC PRECIPITANTS

A brief discussion of the analytical characteristics of the more important organic precipitants is given in the following sections.

*Acetic Acid (Sodium or Ammonium Salt).—*



*Solubility.*—Soluble in water.

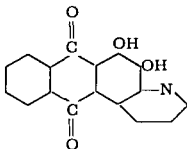
*Reagent.*—A 12–30% aqueous solution.

*Reactions.*—When a neutral solution containing iron(III) ions is boiled with sodium or ammonium acetate, the iron is completely precipitated as basic iron(III) acetate. This reaction has been used principally for the separation of iron from

cobalt, copper, manganese, nickel, and zinc. Aluminum is not precipitated completely when alone, but is precipitated in the presence of iron(III). Ce(IV), thorium, and zirconium are also precipitated from a boiling solution of an acetate, but the method is not applicable to the precipitation of chromium, some rare earths, and uranium.

Sodium is precipitated as a slightly soluble triple acetate with the uranyl ion. (Page 13, vol. I). The precipitate corresponds to the general formula  $\text{NaM}(\text{UO}_2)_3 \cdot (\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}$  in which M represents magnesium, zinc, nickel, and certain other divalent metals. Salts with magnesium and zinc are most satisfactory. Other alkali metals (except lithium) do not interfere. Ammonium, barium, calcium, and magnesium are not precipitated.

*Alizarin Blue.*—

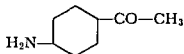


**Solubility.**—Slightly soluble in pyridine; insoluble in water.

**Reagent Solution.**—A saturated solution in pyridine.

**Reactions.**—In a 3 N sulfuric acid solution only the copper(II) ion is precipitated by this reagent.<sup>33</sup> In ammoniacal solution cadmium, nickel, and zinc also precipitate. This is said to be a specific reagent for copper.

*p-Aminoacetophenone.*—

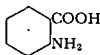


**Solubility.**—Soluble in ether, ethyl alcohol, and water.

**Reagent.**—Dissolve 1 g. of reagent in 100 ml. of 2% ethyl alcohol.

**Reactions.**—Palladium is precipitated by the reagent from a neutral or slightly acidic solution of palladium(II) chloride. This reaction is used to separate palladium from other cations, especially iridium, osmium, platinum, rhodium, and ruthenium, and also gold and iron. Cerium interferes.<sup>34</sup>

*Anthranilic Acid.*—



**Solubility.**—Soluble in acetone, ethyl alcohol, and water.

**Reagent Solution.**—A 1% solution of the acid in water, adjusted with sodium hydroxide to a pH of 6; also a 3% aqueous solution of the sodium salt.

<sup>33</sup> Feigl, F., and Caldas, A., *Anal. Chim. Acta*, 8, 339, 1953.

<sup>34</sup> Schornal, R., *Mikrochemie* 24, 20, 1938; *J. Chem. Soc.*, 1938, 1099; de Hovre, E., *Ing. chim.* 35, 1938.

**Reactions.**—In a slightly acidic or neutral solution the reagent forms insoluble salts with cadmium, cobalt, copper, iron, lead, manganese, mercury(II), nickel, palladium(II), silver, and zinc.<sup>35</sup> Precipitations with anthranilic acid must be made at controlled pH. The range is roughly 3.5 to 5.3 except copper which is reported as 1.4 to 2.8. The reagent is largely limited in use to the precipitation of a single substance from a relatively pure solution, and finds little application in separation procedures.

**Arsonic Acids.**—A number of reagents of the general formula



react selectively with thorium,<sup>36</sup> tin,<sup>37</sup> titanium,<sup>38</sup> and zirconium.<sup>36</sup> Other ions which yield precipitates with these reagents are: bismuth, cerium(IV), hafnium, lead, niobium, tantalum, tungsten(VI), and uranium(IV). The alkali metals, alkaline earth metals, transition elements, and most of the common heavy metals do not form insoluble salts with the arsonic acids in acidic solutions. The arsonic acids most frequently used are phenylarsonic acid, *n*-propylarsonic acid,<sup>39</sup> *p*-hydroxyphenylarsonic acid,<sup>38</sup> and *p*-*n*-butylphenylarsonic acid.<sup>40</sup> These reagents are soluble in ethyl alcohol and water, and are commonly used in 2.5 to 10% aqueous solution, freshly prepared. Under certain conditions the arsonic acids are almost specific reagents for zirconium, but they have also been used for the determination of bismuth, iron, thorium, tin, and titanium.

**Phenylarsonic Acid.**—This reagent is used to precipitate zirconium from a 10% by volume solution of hydrochloric acid.<sup>36</sup> This precipitation may be carried out in the presence of aluminum, beryllium, bismuth, copper, iron(II), manganese(II), nickel, rare earths(III), and zinc. When used for the determination of zirconium in steel,<sup>41</sup> chromium, copper, molybdenum, nickel, thorium, titanium, and vanadium do not interfere, although tin is partially precipitated. The reagent is also used for the determination of thorium,<sup>42</sup> lead,<sup>43</sup> bismuth,<sup>44</sup> and tin.<sup>37, 45</sup>

**Propylarsonic Acid.**—This reagent has been used for the determination of zirconium in steel.<sup>39, 41</sup>

***p*-Hydroxyphenylarsonic Acid.**—This reagent has been recommended for the determination of titanium and zirconium, or zirconium in the presence of titanium.<sup>38</sup> Titanium is precipitated from approximately 0.6 *N* hydrochloric acid or 1.8 *N* sulfuric acid. Zirconium is precipitated from solutions having a normality as high as 3 *N*, and is separated from titanium in the presence of hydrogen peroxide. Titanium(IV) is separated from aluminum, beryllium, calcium, cerium(III), chromium, cobalt, iron, magnesium, manganese, molybdenum, nickel, thallium(III),

<sup>35</sup> Funk, H., and Ditt, M., *Z. anal. Chem.* 91, 332, 1933; 93, 241, 1933; 96, 385, 1934; 123, 241, 1942; Holmes, F., Reed, K. G., and Crimmin, W. R. C., *Anal. Chim. Acta.*, 15, 312, 1956; Shennan, R. J., Smith, J. H. F., and Ward, A. M., *Analyst*, 61, 395, 1936.

<sup>36</sup> Rice, A. C., Fogg, H. C., and James, C., *J. Am. Chem. Soc.*, 48, 895, 1926.

<sup>37</sup> Knapper, J. S., Craig, K. A., and Chandlee, G. C., *J. Am. Chem. Soc.*, 55, 3945, 1933; Kuznetsov, V. I., *J. Applied Chem. (U.S.S.R.)*, 13, 1512, 1940.

<sup>38</sup> Simpson, C. T., and Chandlee, G. C., *Ind. Eng. Chem., Anal. Ed.*, 10, 642, 1938.

<sup>39</sup> Arnold, F. W., and Chandlee, G. C., *J. Am. Chem. Soc.*, 57, 8, 1935.

<sup>40</sup> Craig, K. A., and Chandlee, G. C., *J. Am. Chem. Soc.*, 56, 1278, 1934.

<sup>41</sup> Geist, H. H., and Chandlee, G. C., *Ind. Eng. Chem., Anal. Ed.*, 9, 169, 1937.

<sup>42</sup> Rice, A. C., *U. S. Bur. Mines Rept., Invest. No. 4919*, 13, 1952.

<sup>43</sup> Majumdar, A. K., and Sen Sarma, R. N., *J. Indian Chem. Soc.*, 28, 654, 1951.

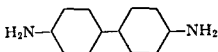
<sup>44</sup> Majumdar, A. K., *J. Indian Chem. Soc.*, 21, 119, 187, 188, 1944; 22, 313, 1945.

<sup>45</sup> Portnov, A. I., *Zhur. Anal. Khim.*, 9, 175, 1954.

uranium(VI), vanadium(IV), and zinc. Tin(IV) is precipitated by this reagent from 0.5 N HCl.<sup>45</sup>

***p*-n-Butylphenylarsonic Acid.**—Iron is precipitated quantitatively from acidic solution in the presence of many ions, including aluminum, beryllium, cadmium, cobalt, copper, erbium, lanthanum, magnesium, manganese, neodymium, nickel, potassium, vanadium, and zinc.<sup>40</sup>

**Benzidine.**—



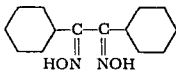
**Solubility.**—Soluble in alcohol and ether; slightly soluble in water. The hydrochloride is soluble in water.

**Reagent Solution.**—Shake 8 g. of benzidine hydrochloride with 1 liter of water and filter. Prepare weekly.

**Reactions.**—Sulfate is precipitated as benzidine sulfate,  $C_{12}H_{12}N_2 \cdot H_2SO_4$ , from a slightly acidic solution which is free from oxidizing agents, but which may contain aluminum, chromium(III), cobalt, copper, iron(II), manganese(II), nickel, and zinc.<sup>46</sup> The precipitate can be weighed, or titrated with standard sodium hydroxide with phenolphthalein as indicator.

The tungstate ion is also precipitated quantitatively from an acidic solution, but the precipitate must be ignited to the oxide for weighing.<sup>47</sup>

**$\alpha$ -Benzildioxime (Diphenylglyoxime).**—

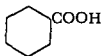


**Solubility.**—Soluble in acetone; slightly soluble in ethyl alcohol; almost insoluble in acetic acid, ether, and water.

**Reagent Solution.**—A 0.02% solution in acetone or ethyl alcohol.

**Reactions.**—Like dimethylglyoxime,  $\alpha$ -benzildioxime forms insoluble compounds with nickel and palladium. This reagent is reported to form a less soluble nickel complex than that with dimethylglyoxime.<sup>48</sup>

**Benzoic Acid.**—



**Solubility.**—Soluble in acetone and ethyl alcohol; slightly soluble in water.

**Reagent Solution.**—Dissolve 10 g. ammonium benzoate in 100 ml. of water; stable in glass containers if thymol is added.

**Reactions.**—In dilute acetic acid solution aluminum, iron(III), and chromium(III) are completely precipitated by boiling with ammonium benzoate.<sup>49</sup> Under the

<sup>46</sup> Raschig, F., Z. angew. Chem., 16, 617, 818, 1903; 19, 331, 1906; Friedheim, C., and Nydegger, O., Z. anal. Chem., 49, 464, 1910.

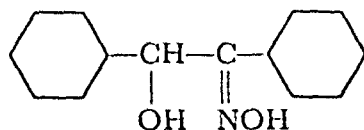
<sup>47</sup> von Knorre, G., Z. anal. Chem., 47, 37, 1908; 49, 461, 1910; Ber., 38, 783, 1905.

<sup>48</sup> Atack, F. W., Chem. Ztg., 27, 773, 1913; Analyst, 38, 316, 1913.

<sup>49</sup> Kolthoff, I. M., Stenger, V. A., and Moskowitz, B., J. Am. Chem. Soc., 56, 812, 1934; Smales, A. A., Analyst, 72, 14, 1947; Osborn, G. H., and Jewsbury, A., Anal. Chim. Acta, 3, 108, 1949.

same conditions ammonium, barium, cadmium, cerium(III), cobalt, iron(II), lithium, magnesium, manganese, mercury(II), nickel, potassium, sodium, strontium, vanadium(IV), and zinc are not precipitated. Bismuth, cerium(IV), tin(IV), titanium(IV), and zirconium are completely precipitated, and beryllium, copper, lead, tin(II), titanium(III), and uranium are partially precipitated. Many important separations have been based on the use of this reagent.<sup>49,50</sup>

$\alpha$ -Benzoinoxime (Cupron).—



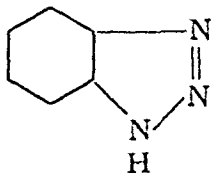
**Solubility.**—Soluble in acetone, ethyl alcohol, and ether; insoluble in water.

**Reagent Solution.**—A 1 or 2% solution in ethyl alcohol. Stable for long periods.

**Reactions.**—Copper is precipitated from an ammoniacal tartrate solution as a green, flocculent compound.<sup>51</sup> This serves to separate copper from aluminum, cadmium, cobalt, iron, lead, nickel, and zinc. The precipitate,  $\text{Cu}(\text{C}_{14}\text{H}_{11}\text{O}_2\text{N})$ , contains 22.01% copper, and may be weighed after drying at 110°C.

Molybdate and tungstate ions are precipitated quantitatively from strongly acidic solutions. Other ions which precipitate completely or partially under the same conditions are chromate, niobate, palladium(II), tantalate, and vanadate. Molybdate<sup>52</sup> and tungstate can be precipitated from a solution containing chromate or vanadate if the latter are first reduced with ferrous sulfate.

Benzotriazole.—



**Solubility.**—Soluble in benzene, ethyl alcohol, and water.

**Reagent Solution.**—A 2% aqueous solution.

**Reactions.**—This reagent has been used for the precipitation of silver,<sup>53</sup> but cadmium, cobalt, copper, iron(II), nickel, and zinc are also precipitated. In the presence of EDTA benzotriazole appears to be a specific precipitant for silver.<sup>54</sup>

The reagent precipitates copper quantitatively from an acetate-tartrate solution of pH 7.0 to 8.5.<sup>55</sup> Other ions that are precipitated under the same conditions are cadmium, cobalt, iron(II), nickel, silver, and zinc. On the other hand, ions that are not precipitated are aluminum, antimony, arsenic, chromium, iron(III), molybdenum(VI), selenium(IV), and tellurium(IV). The reagent is used for making a preliminary separation where interfering ions are present. It may be used to advantage in making a clean separation from antimony, arsenic, molybdenum, selenium, and tellurium, which interfere with the iodometric determination of copper. Osmium is precipitated from an acetic acid-sodium acetate solution.<sup>56</sup>

<sup>50</sup> Jewsbury, A., and Osborn, G. H., *Anal. Chim. Acta*, 3, 642, 1949.

<sup>51</sup> Feigl, F., *Ber.*, 56, 2083, 1923; *Mikrochemie*, 1, 76, 1923.

<sup>52</sup> Knowles, H. B., *Bur. Standards J. Research*, 9, 1, 1932.

<sup>53</sup> Remington, W. J., and Moyer, H. V., *Dissertation Abstr.*, 24, Columbus, Ohio, Ohio State Univ. Press, 1937.

<sup>54</sup> Cheng, K. L., *Anal. Chem.*, 26, 1038, 1954.

<sup>55</sup> Curtis, J. A., *Ind. Eng. Chem., Anal. Ed.*, 13, 349, 1941.

<sup>56</sup> Wilson, R. F., and Baye, L. J., *Talanta*, 1, 351-4, 1958.

**Solubility.**—Soluble in water and hot ethyl alcohol.

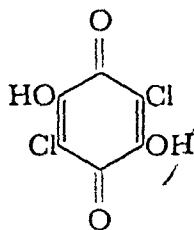
**Reagent Solution.**—A 1% aqueous solution of the potassium salt.

**Reactions.**—This reagent precipitates many ions under various conditions, and has been used in a number of useful analytical separations.<sup>64</sup> Bismuth is precipitated from a 0.1 *N* nitric acid solution. Under these conditions the following ions do not precipitate: alkaline earths; aluminum; beryllium; chromium(III); cobalt; magnesium; manganese; nickel; rare earths; thorium; titanium; uranium; and zirconium. In 0.1 *N* hydrochloric acid cerium(III) and iron(II) do not interfere. At pH 1.5 to 2.5, and in the presence of citrate or tartrate, arsenic(III), cerium(IV), molybdate, and tungstate do not interfere.

In 0.1 *N* hydrochloric or sulfuric acid, arsenic and antimony are precipitated. At pH 6 to 8, and in the presence of citrate or tartrate, cadmium, copper, lead, mercury(II), palladium, silver, and thallium(I) are precipitated. Thallium(I) is precipitated over the pH range 1 to 13; silver from a 0.2 *N* nitric acid solution up to a slightly basic solution; palladium from 0.1 *N* acid to a slightly basic solution; and lead over the pH range 3 to 6.5.

***p*-Bromomandelic Acid.**—This reagent is similar to mandelic acid, but is a more sensitive precipitant for zirconium.<sup>65</sup>

**Chloranilic Acid (2,5-Dichloro-3,6-dihydroxy-1,4-benzoquinone).**—

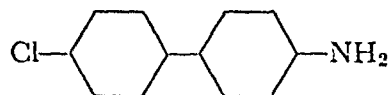


**Solubility.**—Slightly soluble in water.

**Reagent Solution.**—A 0.1% aqueous solution.

**Reactions.**—The reagent forms insoluble compounds with calcium, barium, strontium, copper, and manganese.<sup>66</sup> It also yields precipitates with bismuth, cadmium, cobalt, lead, mercury(II), silver, and zirconium.

**4-Chloro-4'-aminodiphenyl.**—



**Solubility.**—Hydrochloride sparingly soluble in water.

**Reagent Solution.**—Dissolve 2.4 g. of the reagent hydrochloride in 800 ml. of water containing 50 ml. of 1 *N* hydrochloric acid, and dilute to one liter.

**Reactions.**—Like benzidine, this reagent forms an insoluble sulfate. Precipitation is best carried out in a solution of pH 1.0 to 2.0, and the sulfate is said to be less soluble than that of benzidine or diaminotolane.<sup>67</sup> Oxalate, phosphate, selenate, and tellurite also form insoluble salts. Acetate, bromide, chloride, citrate,

<sup>64</sup> Majumdar, A. K., and Singh, B. R., *Z. anal. Chem.*, 154, 262, 413, 1957; 155, 1, 81, 86, 166, 1957; 161, 261, 1958.

<sup>65</sup> Oesper, R. E., and Klingenberg, J. J., *Anal. Chem.*, 21, 1509, 1949.

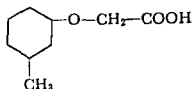
<sup>66</sup> Barretto, A., *Rev. quim. ind. (Rio de Janeiro)*, 15, 16, 1946; Frost-Jones, R. E. U., and Yardley, J. T., *Analyst*, 77, 468, 1952.

<sup>67</sup> Belcher, R., Nutten, A. J., and Stephen, W. I., *J. Chem. Soc.*, 1953, 1334.

iodide, nitrate, and tartrate do not interfere with the sulfate determination. This reagent has also been used as a precipitant for molybdate and tungstate in solutions of pH 1.8 to 2.8 and 1.6 to 2.2, respectively.<sup>68</sup>

*p*-Chloromandelic Acid.—This reagent is similar to mandelic acid, but is a somewhat more sensitive precipitant for zirconium.<sup>69</sup>

*m*-Cresoxyacetic Acid.—



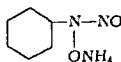
*Solubility*.—Soluble in water.

*Reagent Solution*.—A 2% aqueous solution.

*Reactions*.—From a neutral or slightly acidic solution, the reagent precipitates ions of iron(III), thorium, tin, titanium, and zirconium. In a solution 0.25 *N* in hydrochloric acid, only zirconium is precipitated.<sup>69</sup> Aluminum, barium, beryllium, calcium, the lanthanons, nickel, and uranyl ions do not interfere. Iron(III) is partially precipitated, and sulfate interferes with the zirconium determination.

Thorium is precipitated from a boiling acidic solution of pH 2 to 3.2 in the presence of ammonium nitrate. This reaction is used for the separation of thorium from the rare earths.<sup>70</sup>

*Cupferron (Ammonium nitrosophenylhydroxylamine)*.—



*Solubility*.—Readily soluble in water.

*Reagent Solution*.—Use a freshly prepared, cold, 5 or 6% aqueous solution. The reagent is not very stable.

*Reactions*.—Cupferron was proposed originally for the separation of copper and iron,<sup>71</sup> but has been used for the precipitation of many metals. The elements precipitated by cupferron may be divided into groups as follows:<sup>72</sup>

(a) From weakly acidic or neutral solutions:

*Complete*: aluminum, antimony, beryllium, bismuth, cadmium, cerium, cobalt, copper, gallium, hafnium, indium, iron, lanthanum, lanthanides, molybdenum, niobium, palladium, polonium, scandium, tantalum, thallium, thorium, tin, titanium, tungsten, uranium, vanadium, yttrium, and zirconium.

*Partial*: chromium, gold, lead, manganese, mercury, nickel, silver, and zinc.

(b) From a 10% by volume mineral acid solution:

*Complete*: bismuth, cerium, gallium, hafnium, iron, molybdenum, niobium, palladium, polonium, tantalum, tin, titanium, tungsten, vanadium, and zirconium.

*Partial*: actinium, copper, indium, lanthanum, neodymium, praseodymium, rare earths, thallium, thorium, and uranium.

<sup>68</sup> Liang, Shu-Chuan, and Wang, Shun-Jung, *Hua Hsüeh Hsüeh Pao*, 24, 117, 1958.

<sup>69</sup> Venkatarmaniah, M., and Rao, Bh. S. V. Raghava, *Anal. Chem.*, 23, 539, 1951.

<sup>70</sup> Venkatarmaniah, M., Rao, Bh. S. V. Raghava, and Rao, C. Lakshmana, *Anal. Chem.*, 24, 747, 1952.

<sup>71</sup> Baudisch, O., *Chem. Ztg.*, 33, 1298, 1909.

<sup>72</sup> Cheng, K. L., *Analyst*, 126, 1961.



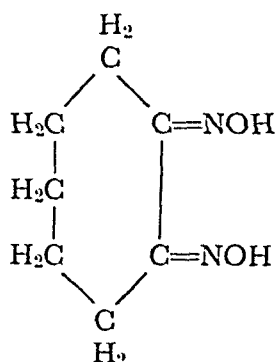
(c) From a solution of pH 5.5, and in the presence of citrate and EDTA:

*Complete:* aluminum, beryllium, cerium, hafnium, iron, niobium, tantalum, tin, titanium, uranium, and zirconium.

*Partial:* rare earths.

Cupferron offers few advantages for the determination of the metals, but it has been widely used in a number of important separations.<sup>73,74</sup> Among these are: (1) group separation of iron, titanium, vanadium, and zirconium in strongly acidic solution from the alkali metals, the alkaline earths, aluminum, arsenic, cobalt, copper, manganese, nickel, phosphorus, and uranium(VI); (2) vanadium from uranium(VI), vanadium from phosphorus, vanadium from tungsten in the presence of fluoride, iron from pure metals such as aluminum and zinc, uranium(VI) from uranium(IV), and niobium and tantalum from various other substances; and (3) the removal of undesirable elements as a preliminary to the determination of various elements by other methods, e.g., iron in the determination of aluminum.

*1,2-Cycloheptanedionedioxime (Heptoxime).—*

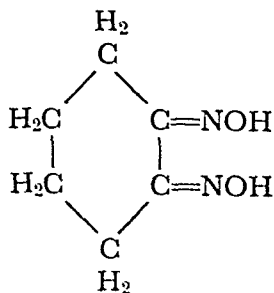


*Solubility.*—Slightly soluble in water.

*Reagent Solution.*—A saturated aqueous solution.

*Reactions.*—This reagent may be used as a precipitant for nickel and palladium in place of dimethylglyoxime.<sup>75,76</sup>

*1,2-Cyclohexanedionedioxime (Nioxime).—*



*Solubility.*—Slightly soluble in water.

*Reagent Solution.*—An 0.8% aqueous solution; stable indefinitely.

<sup>73</sup> Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd Ed., John Wiley and Sons, New York, 1953, 116–22; Lundell, G. E. F., and Knowles, H. B., *J. Ind. Eng. Chem.*, 12, 344, 1920.

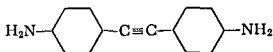
<sup>74</sup> Smith, G. F., *Cupferron and Neo-Cupferron*, G. Frederick Smith Chemical Co., Columbus, Ohio, 1938.

<sup>75</sup> Voter, R. C., and Banks, C. V., *Anal. Chem.*, 21, 1320, 1949.

<sup>76</sup> Ferguson, R. C., Voter, R. C., and Banks, C. V., *Mikrochemie ver. Mikrochim. Acta*, 38, 11, 1951.

**Reactions.**—Like dimethylglyoxime, this reagent is used for the precipitation of nickel and palladium.<sup>77</sup> Quantitative precipitation of nickel occurs at pH 3.0 or higher, and palladium within the range 0.7 to 3.0. It possesses the advantage over dimethylglyoxime of being more soluble in water.

*4,4'-Diaminotolane.*—

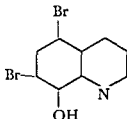


**Solubility.**—Soluble in acetone.

**Reagent Solution.**—Dissolve 1 g. of reagent in 5 ml. of acetone.

**Reactions.**—Like benzidine, 4,4'-diaminotolane precipitates sulfate, but the sulfate of the latter is less soluble than that of benzidine.<sup>78</sup> Precipitation is best carried out at pH 3.0 to 4.0. Chromate and phosphate interfere, but chromium(VI) can be reduced to chromium(III), which does not interfere. Calcium, magnesium, zinc, nitrate, and perchlorate ions do not interfere.

*5,7-Dibromo-8-hydroxyquinoline.*—

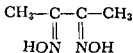


**Solubility.**—Soluble in acetic acid, benzene, and ethyl alcohol; slightly soluble in ether, insoluble in cold water.

**Reagent Solution.**—A 0.5% solution in acetone, or in acetone acidified with hydrochloric or nitric acid.

**Reactions.**—This reagent gives reactions similar to those of 8-hydroxyquinoline. Useful separations have been based on the fact that copper, iron, and titanium are precipitated from solutions of mineral acids.<sup>79,80</sup>

*Dimethylglyoxime.*—



**Solubility.**—Soluble in ethyl alcohol; insoluble in water.

**Reagent Solution.**—A 1% alcoholic solution, which is stable indefinitely, or a 3% solution in 1 N sodium hydroxide.

**Reactions.**—Dimethylglyoxime forms insoluble compounds with bismuth, iron(II), nickel, palladium, and platinum(II).<sup>81</sup> At pH below 5, only nickel and palladium form insoluble compounds. Precipitation of nickel from an ammoniacal tartrate solution may be used to separate this element from a large number of elements

<sup>77</sup> Voter, R. C., Banks, C. V., and Diehl, H., *Anal. Chem.*, 20, 458, 1948.

<sup>78</sup> Belcher, R., Kapel, M., and Nutton, A. J., *Anal. Chim. Acta*, 8, 122, 1953.

<sup>79</sup> Haase, L. W., *Z. anal. Chem.*, 78, 113, 1929.

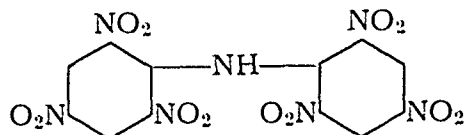
<sup>80</sup> Berg, R., and Kustenmacher, H., *Z. anorg. allgem. Chem.*, 204, 215, 1932.

<sup>81</sup> Diehl, H., *The Applications of the Dioximes to Analytical Chemistry*, G. Frederick Smith Chemical Co., Columbus, Ohio, 1940.

with which it is commonly associated;<sup>82</sup> these include aluminum, antimony, arsenic, bismuth, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, molybdenum, tin, and zinc.

Palladium(II) is precipitated from dilute hydrochloric or sulfuric acid solution. Bismuth, as the chloride or nitrate, when treated with the reagent and made strongly basic with ammonia, gives a voluminous yellow precipitate.<sup>83</sup>

*Dipicrylamine (Hexanitrodiphenylamine).*—

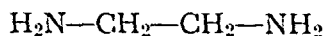


**Solubility.**—Soluble in acetone and ether; slightly soluble in water; insoluble in mineral acids, carbon tetrachloride, chloroform, benzene, and ethyl alcohol.

**Reagent Solution.**—(a) Magnesium dipicrylamine: mix 5 g. of magnesium oxide with 12 g. of reagent and add 400 ml. of water. Stir, let stand 15 to 20 hours, and filter. (b) Sodium dipicrylamine: mix the reagent with a small excess of sodium carbonate, and add water to make a 3% solution.

**Reactions.**—The sodium or magnesium salt of this reagent forms a slightly soluble, red, crystalline precipitate with potassium.<sup>84</sup> Cesium and rubidium also yield precipitates with the reagent, but calcium, lithium, magnesium, and sodium do not. The potassium precipitate is  $\text{KC}_{12}\text{N}_7\text{O}_{12}\text{H}_4$ , and contains 8.194% potassium.

*Ethylenediamine.*—

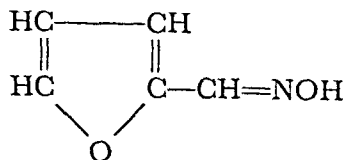


**Solubility.**—Soluble in ethyl alcohol and water; slightly soluble in ether; insoluble in benzene.

**Reagent Solution.**—Use pure ethylenediamine.

**Reactions.**—This reagent reacts with the copper(II) ion to form a complex,  $[\text{Cu}(\text{en})_2]^{++}$ , where  $\text{en} = \text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ . This complex ion forms with the iodo complexes of cadmium and mercury insoluble compounds having the following composition:  $[\text{Cu}(\text{en})_2][\text{CdI}_4]$  and  $[\text{Cu}(\text{en})_2][\text{HgI}_4]$ . These reactions are used to precipitate cadmium, copper, and mercury.<sup>85</sup> Palladium is also precipitated quantitatively as  $[\text{Pd}(\text{en})_2][\text{HgI}_4]$  in the pH range 6 to 8.<sup>86</sup>

*$\beta$ -Furfuraldoxime.*—



**Solubility.**—Soluble in acetone, ethyl alcohol, and water.

**Reagent Solution.**—Dissolve 10 g. of the reagent in 100 ml. of ethyl alcohol.

<sup>82</sup> Brunck, O., Z. angew. Chem., 20, 834, 1907.

<sup>83</sup> Wunder, M., and Thuringer, V., Chem. Ztg. (ii), 550, 1912; Ann. chim. anal. chim. appl. 17, 201, 328, 1912; Z. anal. Chem., 52, 101, 660, 740, 1913.

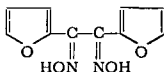
<sup>84</sup> Kolthoff, I. M., and Bendix, G. H., Ind. Eng. Chem. Anal. Ed., 11, 94, 1939; Winkel, A., and Maas, H., Angew. Chem., 49, 827, 1936.

<sup>85</sup> Spacu, G., and Suciut, G., Z. anal. Chem., 77, 334, 1929.

<sup>86</sup> Watt, G. W., Sowards, D. M., and McCarley, R. E., Anal. Chem., 28, 556, 1956.

**Reactions.**—Palladium is precipitated as  $\text{Pd}(\text{C}_4\text{H}_3\text{OCHNOH})_2\text{Cl}_2$  from a solution that is 3% in hydrochloric acid.<sup>87</sup> The following do not interfere: alkali metals; alkaline earth metals; aluminum; antimony; arsenic; bismuth; borate; cadmium; cerium(III); cobalt; chromium; copper; iron(III); manganese; mercury(II); molybdenum(VI); nickel; nitrate; osmium(IV); phosphate; platinum(IV); rhodium(III); ruthenium(III); selenium(IV); sulfate; thorium; tin; titanium(IV); tungstate; vanadium(V); zinc and zirconium. Interfering substances are gold, cerium(IV), and elements whose chlorides are insoluble.

*$\alpha$ -Furildioxime.*—

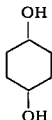


**Solubility.**—Soluble in ether and ethyl alcohol.

**Reagent Solution.**—Dissolve 2 g. of reagent in 100 ml. of hot water, or in sufficient warm ethyl alcohol to form a 10 to 15% solution.

**Reactions.** This reagent is similar to dimethylglyoxime in its reactions with nickel and palladium.<sup>88</sup> The nickel complex is less soluble than that with dimethylglyoxime and has a smaller nickel content. The great advantage of this reagent is its water solubility.

*Hydroquinone.*—

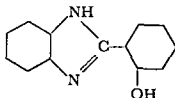


**Solubility.**—Soluble in ether and ethyl alcohol; moderately soluble in water; slightly soluble in benzene.

**Reagent Solution.**—A 1% aqueous solution.

**Reactions.**—In a cold 1.2 *N* solution of hydrochloric acid, gold is reduced and quantitatively precipitated as the free metal by hydroquinone. Platinum and palladium do not interfere.<sup>89</sup> Silver is also precipitated as the metal by this reagent.<sup>90</sup>

*2-(o-Hydroxyphenyl)benzimidazole.*—



<sup>87</sup> Hayes, J. R., and Chandlee, G. C., *Ind. Eng. Chem., Anal. Ed.*, **14**, 491, 1942.

<sup>88</sup> Soule, B. A., *J. Am. Chem. Soc.*, **47**, 981, 1925; Reed, S. A., and Banks, C. V., *Proc. Iowa Acad. Sci.*, **55**, 267, 1948.

<sup>89</sup> Beamish, F. E., Russell, J. J., and Seath, J., *Ind. Eng. Chem., Anal. Ed.*, **9**, 174, 1937.

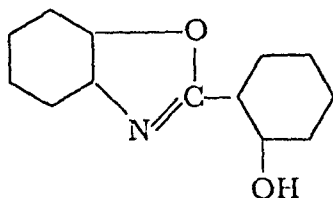
<sup>90</sup> Mitranescu, M., *Acad. rep. populare Romine, Baza cercetari stiint. Timisoara Studii cercetari stiint., Ser. stiinte chim*, **5**, Nos. 3-4, 3, 45, 1958.

**Solubility.**—Soluble in alcohol.

**Reagent Solution.**—Dissolve 1 g. of reagent in 100 ml. of 95% ethyl alcohol.

**Reactions.**—This compound is a selective reagent for mercury. Precipitation is complete in the range pH 6.0 to 7.0, and citrate is used to prevent precipitation of hydroxides.<sup>91</sup> Aluminum, arsenic, barium, bismuth, cadmium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, potassium, silver, sodium, tin(II), and zinc do not form precipitates.

*2-(o-Hydroxyphenyl)benzoxazole.*—



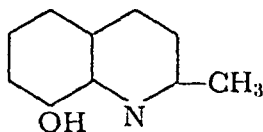
**Solubility.**—Soluble in alcohol.

**Reagent Solution.**—Dissolve 1 g. of the reagent in 100 ml. of 95% ethyl alcohol.

**Reactions.**—This reagent has been used as a precipitant for cadmium.<sup>92</sup> The only common ions which interfere are cobalt, copper, and nickel. Copper precipitates at pH 3.5 to 4.0, and can, therefore, be removed by precipitation in acid solution. Cadmium does not begin to precipitate in the presence of tartrate until pH 6.5, and is best precipitated at pH 11.0 to 12.0. Under these conditions calcium is precipitated as the tartrate.

Palladium may be precipitated by adding the reagent to a slightly acidic solution containing two volumes of ethyl alcohol. Aluminum, copper, iridium(IV), iron(III), magnesium, nickel, osmium, platinum(II), rhodium(II), and zinc do not interfere.<sup>93</sup>

*8-Hydroxyquinaldine (2-methyl-8-hydroxyquinoline).*—



**Solubility.**—Soluble in benzene, ether, and ethyl alcohol; insoluble in water.

**Reagent Solution.**—Dissolve 5 g. of reagent in 12 ml. glacial acetic acid and dilute to 100 ml. with water.

**Reactions.**—This reagent is more selective than 8-hydroxyquinoline.<sup>94</sup> In acetic acid-acetate solution the following ions yield precipitates: bismuth; cadmium; chromium; cobalt; copper; indium; iron; manganese; nickel; silver; titanium(IV); zinc; molybdate; tungstate; and vanadate. Under the same conditions, aluminum, ammonium, barium, beryllium, calcium, lead, magnesium, potassium, and sodium do not precipitate. In the presence of tartrate, bismuth and tin(IV) do not precipitate. In ammoniacal tartrate solution the ions of the above group except aluminum are precipitated, and in addition calcium, lead, magnesium, and strontium are precipitated.

With this reagent it is possible to determine zinc in the presence of aluminum,

<sup>91</sup> Walter, J. L., and Freiser, H., *Anal. Chem.*, **25**, 127, 1953.

<sup>92</sup> Walter, J. L., and Freiser, H., *Anal. Chem.*, **24**, 984, 1952.

<sup>93</sup> Wilson, R. F., and Baye, L. J., *Z. anal. Chem.*, **166**, 359, 1959.

<sup>94</sup> Merritt, L. L., and Walker, J. K., *Ind. Eng. Chem. Anal. Ed.*, **16**, 387, 1944.

and also in the presence of magnesium. It has also been used for the determination of indium.

*8-Hydroxyquinoline (oxine, 8-quinolinol).—*



**Solubility.**—Soluble in acetic acid, acetone, ethyl alcohol, and chloroform; slightly soluble in water.

**Reagent Solution.**—(a) A 3% solution in ethyl alcohol or acetone; should be protected from light. (b) A 2 to 3% solution in 1 to 2 *N* acetic acid. This solution is prepared by adding the solid reagent to glacial acetic acid, and diluting properly with water. This solution is stable indefinitely if stored in amber bottle. For precipitations at high pH, use the alcoholic solution; for low pH, use the acetic acid solution.

**Reactions.**—8-Hydroxyquinoline is a non-selective, though very versatile and useful reagent.<sup>95</sup> Generally, this reagent precipitates the same metals as ammonia. By the proper control of pH, however, a number of important separations can be effected. The ions precipitated by the reagent from two different media are:<sup>96</sup>

(a) From an acetate buffered solution of pH 5.7:

*Complete:* Aluminum, bismuth, cadmium, cobalt, copper, gallium, hafnium, indium, iron, mercury, molybdenum, neptunium, nickel, niobium, palladium, protoactinium, plutonium, silver, tantalum, thorium, titanium, tungsten, uranium, zinc, and zirconium.

*Partial:* Actinium, antimony, chromium, gold, iridium, lanthanum, osmium, rare earths, rhodium, ruthenium, scandium, tin, vanadium, and yttrium.

(b) From ammoniacal solution of pH greater than 7.5.

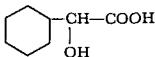
*Complete:* Actinium, aluminum, beryllium, bismuth, cadmium, cerium, copper, gallium, hafnium, indium, iron, lanthanum, magnesium, manganese, mercury, neptunium, niobium, palladium, plutonium, protoactinium, rare earths, scandium, tantalum, thorium, titanium, uranium, yttrium, zinc, and zirconium.

*Partial:* Antimony, barium, calcium, chromium, cobalt, gold, iridium, lead, molybdenum, nickel, osmium, radium, rhodium, ruthenium, silver, strontium, thallium, tin, tungsten, and vanadium.

(c) Not precipitated: antimony(V), arsenic, cesium, germanium, platinum, polonium, potassium, rhenium, rubidium, selenium, sodium, tellurium, and thallium(I).

8-Hydroxyquinoline is useful for the determination of a number of metals, and is also useful in many important analytical separations. Examples of these are: aluminum from beryllium; magnesium from the alkali and alkaline earths, from bismuth, iron, manganese, nickel, and zinc; and zinc from the alkali and alkaline earths, from antimony, arsenic, chromium, lead, manganese, and uranium.

*Mandelic Acid.*—



<sup>95</sup> Berg, R., *Z. anal. Chem.*, 70, 341, 1927; 71, 23, 171, 321, 369, 1927; 72, 177, 1927; 76, 191, 1929. Also Berg, R., *Das o-Oxychinolin (oxin)*, F. Enke, Stuttgart, 1936; Hollingshead, R. G. W., *Oxine and Its Derivatives*, 4 vols., Butterworths, London, 1954.

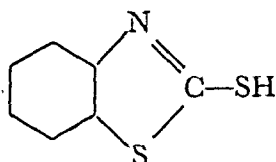
<sup>96</sup> Hoffman, J. I., *Chemist-Analyst*, 49, 126, 1960.

**Solubility.**—Soluble in ether, ethyl alcohol, and water.

**Reagent Solution.**—A 2% aqueous solution.

**Reactions.**—The reagent has been used principally to precipitate zirconium from a hydrochloric acid solution without interference from aluminum, antimony, barium, bismuth, cadmium, calcium, cerium, chromium, cobalt, copper, iron, magnesium, manganese, mercury, nickel, thorium, tin, titanium, uranium, vanadium, or zinc. Hafnium also precipitates under the same conditions.<sup>97</sup> Mandelic acid has also been used to precipitate plutonium,<sup>98</sup> scandium,<sup>99</sup> and the rare earths.<sup>100</sup>

*Mercaptobenzothiazole (Kaptax, Vulcacit-mercapto).*—

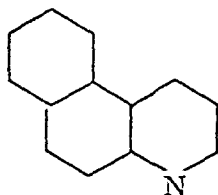


**Solubility.**—Slightly soluble in ethyl alcohol, aqueous sodium hydroxide, and glacial acetic acid; insoluble in water.

**Reagent Solution.**—A 5% solution in ethyl alcohol or an aqueous solution in 1 N sodium hydroxide.

**Reactions.**—This reagent forms insoluble compounds with many metals; these are aluminum, beryllium, bismuth, cadmium,<sup>101</sup> copper,<sup>101</sup> gold, iridium,<sup>102</sup> lead, mercury, palladium,<sup>103</sup> platinum,<sup>103</sup> rhodium,<sup>104</sup> scandium,<sup>105</sup> silver, thallium, thorium, and zirconium. In a weakly acidic solution, however, only copper of the common metals is precipitated. This makes possible the separation of copper from the alkali metals, the alkaline earth metals, cadmium, cobalt, manganese, nickel, and zinc.<sup>101</sup> Platinum and palladium are also precipitated from an acidic solution.<sup>103</sup> Cadmium is precipitated from an ammoniacal solution.<sup>101</sup>

*β-Naphthoquinoline (5,6-naphthoquinoline).*—



**Solubility.**—Soluble in ether, ethyl alcohol, and benzene; insoluble in water.

**Reagent Solution.**—A 2.5% solution in 0.5 N sulfuric acid.

**Reactions.**—The reagent precipitates in strong mineral acid solution the ions of bismuth, cadmium, copper, iron(III), mercury, uranium, and zinc. These ions are precipitated as complex anions. The stability and insolubility increase in the

<sup>97</sup> Kumins, C. A., *Ind. Eng. Chem., Anal. Ed.*, 19, 376, 1947; Hahn, R. B., *Anal. Chem.*, 21, 1579, 1949.

<sup>98</sup> Merz, E., *Z. anal. Chem.*, 166, 417, 1959.

<sup>99</sup> Alimarin, I. P., and Shen, Khan-Si, *Zhur. Anal. Khim.*, 15, 31, 1960.

<sup>100</sup> Weaver, B., *Anal. Chem.*, 26, 476, 1954.

<sup>101</sup> Spacu, G., and Kuras, M., *Z. anal. Chem.*, 102, 24, 108, 1935; 104, 88, 1936.

<sup>102</sup> Barefoot, R. R., McDonnell, W. J., and Beamish, F. E., *Anal. Chem.*, 23, 514, 1951.

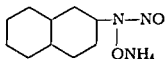
<sup>103</sup> Ubaldini, I., and Nebbia, L., *Ann. chim. applicata*, 38, 241, 1948; *Gazz. chim. ital.*, 78, 293, 1948.

<sup>104</sup> Haines, R. L., and Ryan, D. E., *Can. J. Research*, 27B, 72, 1949.

<sup>105</sup> Pirtea, T. I., *Rev. Chim. (Roumania)*, 11, 336, 1960.

order: Cl, Br, I, SCN. In the presence of chloride ions, only bismuth and mercury are precipitated, with bromide or iodide, bismuth, cadmium, and mercury are precipitated; in the presence of nitric or sulfuric acid, uranium and iron(III) are precipitated as the thiocyanate complexes. The reagent is useful for the separation of cadmium from zinc, and from antimony and zinc.<sup>106</sup> Germanium has also been precipitated as the trioxalatogermanate.<sup>107</sup> Both molybdate and tungstate are precipitated by the reagent from an acidic solution.<sup>108</sup> Tungstate precipitates from a strongly acidic solution while molybdate precipitates from a weakly acidic solution; hence, these two ions can be separated by a regulation of the acidity of the solution.

*Neocupferron (α-Nitrosanaphthylhydroxylamine, ammonium salt).—*

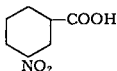


**Solubility.**—Soluble in water.

**Reagent Solution.**—Use a 6% aqueous solution; solution not stable.

**Reactions.**—Neocupferron gives many of the reactions of cupferron, but the iron and copper salts appear to be less soluble and more bulky than the corresponding cupferrides. The reagent has been used for the precipitation of traces of iron and copper from water without preliminary concentration.<sup>109</sup>

*m-Nitrobenzoic Acid.*—



**Solubility.**—Soluble in ether and ethyl alcohol; slightly soluble in water.

**Reagent Solution.**—A saturated aqueous solution.

**Reactions.**—Thorium is quantitatively precipitated by *m*-nitrobenzoic acid at pH greater than 2.4. This affords a method for the separation of thorium from cerium, lanthanum, praseodymium, and neodymium.<sup>110</sup> Thorium can be separated from uranium by precipitating at pH 2.6 to 2.8. Other elements precipitated by the reagent are cerium(IV), mercury, plutonium(IV), and zirconium. Cerium(III) and plutonium(III) are not precipitated. Tin salts hydrolyze to yield a precipitate.

By a careful control of acidity, *m*-nitrobenzoic acid is a selective reagent for zirconium.<sup>111</sup> Thorium is completely precipitated from 0.02 *N* nitric acid, but is not precipitated from 0.1 *N* nitric acid or greater. Zirconium, however, is completely precipitated from 0.2 *N* nitric acid; thus thorium and zirconium can be separated by precipitation from 0.2 *N* nitric acid.

<sup>106</sup> Berg, R., and Wurm, O., Ber., 60B, 1664, 1927, Pass, A., and Ward, A. M., Analyst, 58, 667, 1933; Hecht, F., and Reissner, R., Z. anal. Chem., 103, 88, 1935.

<sup>107</sup> Willard, H. H., and Zuehlke, C. W., Ind. Eng. Chem., Anal. Ed., 16, 322, 1944.

<sup>108</sup> Golubtsova, R. B., and Shemyakin, F. M., Zhur. Anal. Khim., 3, 118, 1948; 4, 232, 1949; Platonov, B. A., Vestnik Leningrad, Univ., 7, No. 12, Ser. Mat., Fiz., i Khim., 137, 1952.

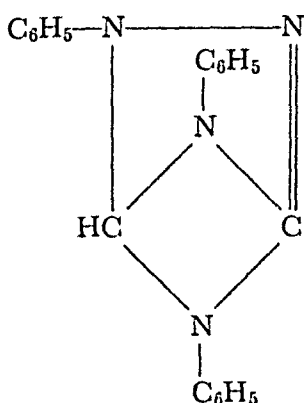
<sup>109</sup> Baudisch, O., and Holmes, S., Z. anal. Chem., 119, 241, 1940.

<sup>110</sup> Neish, A. C., J. Am. Chem. Soc., 26, 780, 1904; Kolbe, A., and Ahrle, H., Z. angew. Chem., 18, 92, 1905.

<sup>111</sup> Osborn, G. H., Analyst, 73, 381, 1948.



*Nitron (4,5-Dihydro-1,4-diphenyl-3,5-phenylimino-1,2,4-triazole).—*

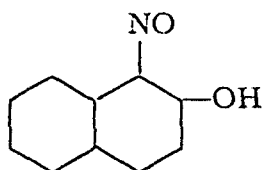


**Solubility.**—Soluble in acetone, benzene, chloroform, and ethyl alcohol; insoluble in water.

**Reagent Solution.**—Dissolve 10 g. nitron in 100 ml. of 5% acetic acid; protect from light.

**Reactions.**—Nitron is used to precipitate nitrate,<sup>112</sup> perchlorate,<sup>113</sup> perrhenate,<sup>114</sup> fluoborate,<sup>115</sup> and tungstate<sup>116</sup> ions. Other ions which may yield precipitates are bromide, chlorate, chromate, iodide, nitrite, and thiocyanate. Its most important use is for the precipitation of nitrate, which separates as  $C_{20}H_{16}N_4 \cdot HNO_3$ , and perrhenate, which forms as  $C_{20}H_{16}N_4 \cdot HReO_4$ .

*1-Nitroso-2-naphthol.*—



**Solubility.**—Soluble in acetic acid, benzene, and ethyl alcohol; insoluble in water.

**Reagent Solution.**—Use a saturated solution of the reagent in 50% acetic acid.

**Reactions.**—This reagent precipitates quantitatively from a slightly acidic solution the following ions: cobalt; copper; iron(III); palladium; and zirconium. Other ions which are partially precipitated are bismuth, chromium(III), silver, tin, titanium, tungsten, uranium, and vanadium. Ions that are not precipitated are aluminum, antimony, arsenic, beryllium, cadmium, calcium, lead, magnesium, manganese, mercury, nickel, and zinc. The alkali and alkaline earth metals and phosphate do not yield precipitates. The most important use for this reagent is for the separation of cobalt from large amounts of nickel after prior removal of iron.<sup>117</sup> Cobalt is precipitated as  $(C_{10}H_6O_2N)_3Co$ .

<sup>112</sup> Busch, M., Ber., 38, 861, 1905; Gutbier, A., Z. angew. Chem., 18, 494, 1905.

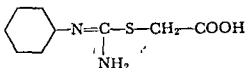
<sup>113</sup> Leobich, O., Z. anal. Chem., 68, 34, 1926.

<sup>114</sup> Geilmann, W., and coworkers, Z. anorg. allgem. Chem., 193, 311, 1930; 195, 289, 1931; 199, 347, 1931; 249, 225, 1942.

<sup>115</sup> Berkovich, V. L., and Kulyashev, Y. V., J. Applied Chem. (U.S.S.R.), 10, 192, 1937.

<sup>116</sup> Gutbier, A., and Weise, G. L., Z. anal. Chem., 53, 426, 1914.

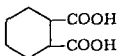
<sup>117</sup> Knorre, G., Z. angew. Chem., 16, 677, 1904; Schmidt, W., Z. anorg. allgem. Chem., 80, 335, 1913; Krauss, F., and Dencke, H., Z. anal. Chem., 67, 86, 1925; Mayr, C., Z. anal. Chem., 98, 402, 1934.

*Phenylthiohydantoic Acid.*—

**Solubility.**—Soluble in acetone, ether, and ethyl alcohol; slightly soluble in water.

**Reagent Solution.**—A saturated aqueous solution.

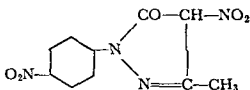
**Reactions.**—In solutions slightly acidified with acetic acid, the reagent precipitates antimony, bismuth, cadmium, copper, lead, and mercury quantitatively, while arsenic, tin, and metals not in the hydrogen sulfide group are not precipitated. From a hot, slightly ammoniacal solution, the reagent separates cobalt quantitatively in one operation from aluminum, arsenic, calcium, chromium, magnesium, manganese, molybdenum, titanium, tungsten, uranium, vanadium, and zinc.<sup>118</sup> Iron is kept in solution with citrate. Nickel is partially precipitated.

*Phthalic Acid.*—

**Solubility.**—Soluble in ethyl alcohol; slightly soluble in water and ether.

**Reagent Solution.**—Use a 4% aqueous solution; use boiling hot.

**Reactions.**—This reagent precipitates zirconium quantitatively from solutions up to 0.35 *N* in hydrochloric acid.<sup>119</sup> If the acidity is adjusted to 0.3 *N* in hydrochloric acid, zirconium can be separated from aluminum, beryllium, cerium, iron, manganese, nickel, rare earths, thorium, and uranium. Separation from tin, chromium, titanium, and vanadium requires a second precipitation. Only iron, thorium, tin, and titanium precipitate from a neutral solution.

*Picrolonic Acid (1-p-nitrophenyl-3-methyl-4-nitropyrazol-5-one).*—

**Solubility.**—Soluble in ethyl alcohol; moderately soluble in water.

**Reagent Solution.**—Use of 0.01 *M* aqueous solution; stable for moderate length of time.

**Reactions.**—The reagent forms insoluble picrolonates with barium, calcium, copper, iron, lead, magnesium, manganese, strontium, thorium, and zinc. Procedures have been described for the determination of calcium,<sup>120</sup> lead,<sup>121</sup> and thorium.<sup>122</sup> Calcium is precipitated as  $\text{Ca}(\text{C}_{10}\text{H}_7\text{N}_4\text{O}_5)_2$  at pH 4 to 6. Lead is precipitated at pH 2 to 6.5, and thorium at pH 2 to 3.2. Manganese can be separated from aluminum, chromium, iron, and titanium with this reagent.<sup>123</sup>

<sup>118</sup> Willard, H. H., and Hall, D., *J. Am. Chem. Soc.*, 44, 2219, 2226, 2237, 2253, 1922.

<sup>119</sup> Purushottam, A., and Rao, B. S. V. Raghava, *Analyst*, 75, 684, 1950.

<sup>120</sup> Dworak, R., and Reich-Rohrwig, W., *Z. anal. Chem.*, 86, 98, 1931.

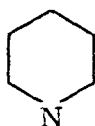
<sup>121</sup> Hecht, F., Reich-Rohrwig, W., and Brantner, H., *Z. anal. Chem.*, 95, 152, 1933.

<sup>122</sup> Hecht, F., and Ehrmann, W., *Z. anal. Chem.*, 100, 87, 1935.

<sup>123</sup> Gusev, S. I., *Zhur. Anal. Khim.*, 1, 114, 1946.

*Propylenediamine.*—

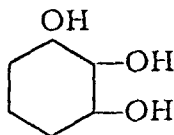
This reagent is used in a manner similar to that for ethylenediamine.<sup>124</sup> Silver is precipitated with this reagent as the  $[\text{AgI}_2]^-$  complex.<sup>125</sup>

*Pyridine.*—

**Solubility.**—Soluble in ether, ethyl alcohol, and water.

**Reagent Solution.**—Pure pyridine used.

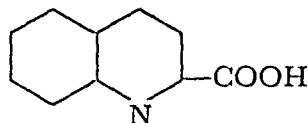
**Reactions.**—In the presence of thiocyanate ions, pyridine forms insoluble compounds with cadmium, cobalt, copper, manganese, nickel, and zinc.<sup>126</sup> These compounds have the composition:  $\text{Co}(\text{SCN})_2\text{Py}_4$ ,  $\text{Mn}(\text{SCN})_2\text{Py}_4$ ,  $\text{Ni}(\text{SCN})_4\text{Py}_4$ ,  $\text{Cd}(\text{SCN})_2\text{Py}_2$ ,  $\text{Cu}(\text{SCN})_2\text{Py}_2$ , and  $\text{Zn}(\text{SCN})_2\text{Py}_2$ , where  $\text{Py} = \text{C}_5\text{H}_5\text{N}$ . Precipitation is carried out by adding potassium thiocyanate and pure pyridine to a neutral or faintly acidic solution of the metal ions. Alkali, alkaline earth metals, and magnesium do not interfere. Lead gives a precipitate of basic thiocyanate. This reagent is useful for the separation of mercury from cadmium, copper, iron, and nickel. Iron is precipitated as the hydroxide.

*Pyrogallol.*—

**Solubility.**—Soluble in ether, ethyl alcohol, and water; slightly soluble in benzene and chloroform.

**Reagent Solution.**—A 3% solution in air-free water or a solid reagent is used.

**Reactions.**—The reagent forms insoluble compounds with antimony<sup>127</sup> and bismuth.<sup>128</sup> It is used for the separation of antimony from arsenic and for the separation of bismuth from lead. It is also used for the determination of antimony and bismuth in the presence of arsenic, cadmium, lead, or zinc.

*Quinaldinic Acid (Quinaldic Acid).*—

**Solubility.**—Soluble in ether, ethyl alcohol, and water.

**Reagent Solution.**—A 1 to 3% aqueous solution of the acid or its sodium salt; stable several weeks when stored in an amber bottle.

**Reactions.**—The reagent forms insoluble salts with cadmium, cobalt, copper, iron(II), iron(III), lead, manganese, mercury(I), mercury(II), molybdate, nickel,

<sup>124</sup> Spacu, G., and Spacu, P., Z. anal. Chem., 89, 187, 1932.

<sup>125</sup> Spacu, G., and Spacu, P., Z. anal. Chem., 90, 182, 1932.

<sup>126</sup> Spacu, G., and Dick, J., Z. anal. Chem., 71, 97, 442, 1927; 74, 188, 1928; 76, 273, 1929.

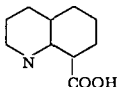
<sup>127</sup> Feigl, F., Z. anal. Chem., 64, 41, 1924.

<sup>128</sup> Feigl, F., and Ordelt, H., Z. anal. Chem., 65, 448, 1924.

palladium(II), platinum(II), silver, thorium, tungstate, zinc, and zirconium.<sup>129</sup> Basic salts of aluminum, beryllium, chromium(III), iron(III), and titanium are also formed. The reagent is used to separate zinc from aluminum, beryllium, chromium, iron, titanium, and uranium in an ammoniacal tartrate solution; zinc from barium, calcium, magnesium, manganese, and phosphate in dilute acetic acid solution; copper from cadmium, cobalt, manganese, and nickel, from dilute sulfuric acid solution; and copper from arsenic, lead, and phosphate from dilute acetic acid.

Copper is precipitated from a relatively acidic solution, while cadmium and zinc remain in solution. Palladium is precipitated from a hot solution of pH 3 to 7 containing ammonium chloride and tartaric acid.<sup>130</sup> No common ions interfere. Thorium and zirconium yield precipitates at pH 2.7 and 3.<sup>130</sup> This method can be used to separate thorium from arsenic, cerium, lanthanum, manganese, mercury, neodymium, praseodymium, and yttrium. Zirconium is not precipitated from a cold but is precipitated from a hot solution. Uranium is also precipitated.<sup>131</sup>

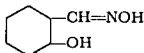
**Quinoline-8-Carboxylic Acid.**—



**Solubility.**—Soluble in acetone, ether, and ethyl alcohol; slightly soluble in water.  
**Reagent Solution.**—A saturated aqueous solution.

**Reactions.**—Copper is precipitated from an acetic acid solution of pH 3.5 to 4 by the reagent. Under the same conditions cadmium, cobalt, lead, mercury, nickel, and zinc do not precipitate. Silver and gold also yield precipitates with this reagent.<sup>132</sup> Cadmium can be separated from antimony, arsenic, bismuth, and copper by precipitating from a dilute sulfuric acid solution containing tartrate.<sup>133</sup> Iron(II) is also precipitated in the presence of tartrate.

**Salicylaldoxime.**—



**Solubility.**—Soluble in acetone, ether, and ethyl alcohol; slightly soluble in water.

**Reagent Solution.**—Dissolve 1 g. of the reagent in 5 ml. of ethyl alcohol, and pour slowly, with stirring, into 95 ml. of water at 86°C.

**Reactions.**—Salicylaldoxime is used for the precipitation and determination of bismuth,<sup>134</sup> copper,<sup>135</sup> lead,<sup>136</sup> nickel,<sup>137</sup> palladium,<sup>138</sup> and zinc. The pH at which

<sup>129</sup> Ray, P., and Bose, M. K., *Z. anal. Chem.*, **95**, 400, 1934; **100**, 324, 1935; *Mikrochemie*, **17**, 11, 1935; Ray, P., and Gupta, J., *Mikrochem.*, **17**, 14, 1935; **18**, 89, 1935.

<sup>130</sup> Majumdar, A. K., and Gupta, J. G. Sen, *Z. anal. Chem.*, **161**, 104, 1958; **162**, 262, 1958.

<sup>131</sup> Erämetsä, O., *Suomen Kemistilehti*, **17B**, 30, 1944.

<sup>132</sup> Gilbreath, J. R., and Haendler, H. M., *Ind. Eng. Chem., Anal. Ed.*, **14**, 866, 1942.

<sup>133</sup> Majumdar, A. K., *J. Indian Chem. Soc.*, **18**, 419, 1941; **22**, 309, 1945.

<sup>134</sup> Flagg, J. F., and Furman, N. H., *Ind. Eng. Chem., Anal. Ed.*, **12**, 529, 663, 1940.

<sup>135</sup> Ephraim, F., **63**, 1928, 1930; **64**, 1012, 1215, 1931; Reif, W., *Mikrochemie*, **9**, 424, 1931; Hecht, F., and Reissner, R., *Mikrochemie*, **17**, 127, 1935.

<sup>136</sup> Ligett, W. B., and Biefeld, L. P., *Ind. Eng. Chem., Anal. Ed.*, **13**, 813, 1941; Ishibashi, M., and Kishi, H., *Bull. Chem. Soc. (Japan)*, **10**, 362, 1935.

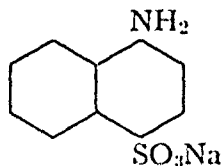
<sup>137</sup> Riley, H., *J. Chem. Soc.*, 1933, 895.

<sup>138</sup> Holzer, H., *Z. anal. Chem.*, **95**, 392, 1933; Gahide, M., *Bull. soc. chim. Belg.*, **45**, 9, 1936.

precipitation is carried out is important in effecting a number of useful separations. Copper is completely precipitated at pH 2.6; nickel begins to precipitate at pH 3.3; bismuth from 7.2 to 9.4; and lead precipitates completely at pH 8.9 or above. In a strongly ammoniacal solution, lead can be separated from cadmium, silver, and zinc. Palladium(II) is precipitated from an acidic solution, and can be separated from platinum. Vanadium is only partially precipitated from a sulfuric acid solution.

The principal use of this reagent has been for the precipitation of copper, which is carried out with very little interference from other ions when the pH of the solution is 2.6.

*Sodium Naphthionate.*—

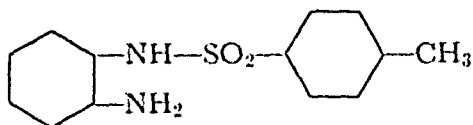


*Solubility.*—Soluble in water.

*Reagent Solution.*—A 10% aqueous solution.

*Reactions.*—Thorium can be separated from associated cerium earth elements by a single precipitation with this reagent.<sup>139</sup> The acidity must be maintained within the narrow limits pH 2.3 to 3.2. Cerium earth metals can be determined in the filtrate by making basic with ammonia, filtering, washing, and igniting.

*T-Sulfonamidine (o-(p-Toluylsulfonamide)aniline).*—



*Solubility.*—Soluble in ethyl alcohol and water.

*Reagent Solution.*—Dissolve 1 g. of reagent in 140 ml. of 95% ethyl alcohol and add 60 ml. of water.

*Reactions.*—Copper is quantitatively precipitated by the reagent from solutions of pH 6.2 to 8.5 as  $\text{Cu}(\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}_2\text{S})_2$ .<sup>140</sup> At pH 6.5 the following ions do not precipitate: barium; beryllium; cadmium; calcium; chromium(III); cobalt; iridium(IV); magnesium; manganese; nickel; strontium; yttrium(III); and zinc. Antimony, bismuth, and silver are removed as chlorides, and metals that tend to precipitate as hydroxides are masked by tartrate.

*Tannin (Tannic Acid).*—

*Solubility.*—Soluble in ethyl alcohol and water; insoluble in chloroform and ether.

*Reagent Solution.*—A 2% aqueous solution, freshly prepared.

*Reactions.*—Tannin has proved extremely useful for the separation and determination of many metals, including aluminum, beryllium, gallium, germanium, molybdenum, niobium, tantalum, titanium, tungsten, and uranium. Many other metals such as antimony, bismuth, lead, tin, and zirconium are partially precipitated as white solids which are readily soluble in dilute acids. A number of metals either give no reaction with tannin, or react only on addition of a base.

<sup>139</sup> Purushottam, A., and Rao, B. S. V. R., *Analyst*, **75**, 555, 1950; Miner, H. S., *U. S. Bur. Mines, Bull.* No. 212, 53, 1923.

<sup>140</sup> Billman, J. H., Janetos, N. S., and Chernin, R., *Anal. Chem.*, **32**, 1342, 1960.

These include: the alkaline earths; cadmium; cerium; cobalt; copper; magnesium; manganese; nickel; platinum; rare earths; thorium; and zinc. These precipitation procedures are used in combination with a variety of reagents, such as acetic, oxalic, salicylic, and tartaric acids or their salts. They also require a fairly careful adjustment of the pH of the solution, and are carried out in hot solutions containing an electrolyte.<sup>141</sup> From an ammoniacal solution, ions of aluminum, beryllium, manganese, niobium, rare earths, tantalum, titanium, uranium, and zirconium are precipitated. For the precipitation of titanium, vanadium, and zirconium, and probably also chromium, iron, niobium, tantalum, thorium, and uranium, from a tartrate solution, the pH should be between 6 and 7.

The metals have been classified into groups depending on their precipitation behavior with tannin. These are as follows: *Group A* includes metals precipitated by tannin from a weakly acidic oxalate solution that is half saturated with ammonium chloride; these are niobium, tantalum, and titanium. *Group B* includes metals precipitated by tannin from a neutral tartrate solution containing an alkali acetate; these are aluminum, chromium, gallium, hafnium, iron, thorium, uranium, and zirconium. *Group C* consists of those elements precipitated by tannin from an ammoniacal tartrate solution; these are beryllium, manganese, and the rare earths.

Important separation procedures in which tannin is used are: niobium and tantalum,<sup>142</sup> niobium and tantalum from aluminum, thorium, and zirconium;<sup>143</sup> titanium from zirconium;<sup>144</sup> uranium from niobium, tantalum, and titanium;<sup>145</sup> aluminum from beryllium;<sup>146</sup> gallium from beryllium, cadmium, cobalt, manganese, nickel, thorium, and zinc;<sup>147</sup> beryllium from aluminum, chromium, iron, thorium, titanium, vanadium, and zirconium;<sup>148</sup> and also tin;<sup>149</sup> germanium from aluminum, iron, thorium, and zirconium;<sup>148</sup> and zirconium from niobium and tantalum.<sup>149</sup>

#### *Tetraphenylarsonium Chloride.*—



**Solubility.**—Soluble in water.

**Reagent Solution.**—0.01 to 0.03 M in water.

**Reactions.**—The reagent forms insoluble salts with bromide, chromate, fluoride, iodate, iodide, molybdate, perchlorate, periodate, permanganate, perbromate, thiocyanate, and tungstate.<sup>150</sup> It also precipitates the halide complexes of such metals as bismuth, cadmium, gold(III), iron(III), mercury(II), platinum(IV), thal-

<sup>141</sup> Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, John Wiley and Sons, New York, 1953.

<sup>142</sup> Powell, A. R., and Schoeller, W. R., *Analyst*, 50, 485, 1925; Schoeller, W. R., *Analyst*, 57, 750, 1932; Schoeller, W. R., *The Analytical Chemistry of Tantalum and Niobium*, Chapman and Hall, London, 1937.

<sup>143</sup> Schoeller, W. R., and Webb, H. W., *Analyst*, 58, 143, 1933.

<sup>144</sup> Powell, A. R., and Schoeller, W. R., *Analyst*, 55, 605, 1930.

<sup>145</sup> Moser, L., and Niessner, M., *Monatsh.*, 48, 113, 1927; Moser, L., and Singer, J., *Monatsh.*, 48, 673, 1927.

<sup>146</sup> Moser, L., and Brukl, A., *Monatsh.*, 50, 657, 1928.

<sup>147</sup> Moser, L., and List, F., *Monatsh.*, 51, 1133, 1929.

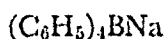
<sup>148</sup> Holness, G., *Anal. Chim. Acta*, 2, 254, 1948.

<sup>149</sup> Schoeller, W. R., and Waterhouse, E. F., *Analyst*, 53, 515, 1928; Schoeller, W. R., and Powell, A. R., *Analyst*, 57, 550, 1932.

<sup>150</sup> Willard, H. H., and Smith, G. M., *Ind. Eng. Chem., Anal. Ed.*, 11, 186, 269, 1939.

lithium(III), tin(IV), and zinc, and also that of tellurium.<sup>151</sup> The reagent has been used for the determination of cadmium, mercury(II), tellurium, thallium,<sup>152</sup> tin(IV), zinc, perchlorate, periodate, permanganate, perbromate, and tungstate.<sup>153</sup>

*Tetraphenylboron (Sodium Salt).—*



*Solubility.*—Soluble in water.

*Reagent Solution.*—A 2 to 3% or 0.1 M aqueous solution; should be prepared every few days.

*Reactions.*—This reagent has been used principally for the determination of potassium,<sup>154</sup> but other ions which form precipitates are ammonium, cesium, rubidium, copper(I), mercury(I),<sup>155</sup> silver, and thallium(I).<sup>156</sup> Procedures have been developed for the determination of these ions also. Copper has been separated from a large number of cations, except mercury(II), by the homogeneous precipitation of copper(I) tetraphenylborate, using ascorbic acid as a reducing agent.<sup>157</sup> EDTA may be used to eliminate interference in some precipitations. Ions which do not interfere are aluminum, barium, calcium, cadmium, cobalt, copper(II), iron(III), lithium, magnesium, nickel, sodium, strontium, zinc, chloride, bromide, iodide, acetate, nitrate, perchlorate, and sulfate.

*Thioacetamide.*—

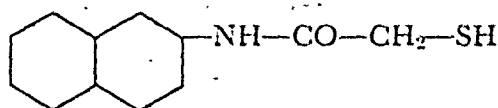


*Solubility.*—Soluble in ethyl alcohol and water; slightly soluble in ether.

*Reagent Solution.*—A 2 or 5% aqueous solution.

*Reactions.*—Thioacetamide hydrolyzes in aqueous solution to form hydrogen sulfide, and has been extensively used to precipitate metal sulfides. Procedures have been described for the precipitation of antimony, arsenic, bismuth, cadmium, copper, lead, mercury, molybdenum, and tin.<sup>158</sup>

*Thionalide (Thioglycolic  $\beta$ -aminonaphthalide).*—



*Solubility.*—Soluble in acetone, ethyl alcohol, and glacial acetic acid; insoluble in water and solutions of mineral acids.

*Reagent Solution.*—A 1 or 2% solution in acetone, ethyl alcohol, or glacial acetic acid; this solution should be freshly prepared.

<sup>151</sup> Bode, H., Z. anal. Chem., 134, 100, 1951.

<sup>152</sup> Smith, Jr., W. T., Anal. Chem., 20, 937, 1948.

<sup>153</sup> Looney, W. C., Univ. Microfilms, Pub. No. 6468; Dissertation Abstracts, 13, 974, 1953.

<sup>154</sup> Wittig, G., and coworkers, Ann., 563, 118, 126, 1949; Raff, P., and Brotz, W., Z. anal. Chem., 133, 241, 1951.

<sup>155</sup> Heyrovsky, A., Analyst, 85, 432, 1960.

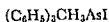
<sup>156</sup> Wendlandt, W. W., Anal. Chim. Acta, 16, 216, 1957.

<sup>157</sup> Davis, D. G., Anal. Chem., 32, 1321, 1960.

<sup>158</sup> Flaschka, H., and Jakobljevich, H., Anal. Chim. Acta, 4, 247, 351, 356, 482, 486, 602, 605, 1950; 5, 60, 152, 1951; Broad, W. C., and Barnard, Jr., A. J., Thioacetamide as a Sulfide Precipitant, Product Bulletin 104, J. T. Baker Chemical Co., Phillipsburg, N. J., 1960.

**Reactions.**—This reagent forms slightly soluble compounds with most of the metals of the hydrogen sulfide group.<sup>150</sup> Elements precipitated by thionalide under different conditions are grouped as follows: (1) from dilute mineral acids—antimony, arsenic, bismuth, copper, gold, mercury, palladium, platinum, ruthenium, silver, and tin; (2) from acetic acid or buffered solution—in addition to the elements of group I, cadmium, cobalt, manganese, and thallium are also precipitated; (3) from an ammoniacal solution containing cyanide and tartrate, only thallium; (4) from a carbonate solution containing tartrate—cadmium, copper, gold, mercury(II), and thallium(I); (5) from a carbonate solution containing cyanide and tartrate—antimony, bismuth, gold, lead, thallium, and tin.

*Triphenylmethylarsonium Iodide.*—



**Solubility.**—Soluble in 95% ethyl alcohol and 0.5% potassium iodide solution.

**Reagent Solution.**—A 0.5% solution in 0.5% potassium iodide.

**Reactions.**—This reagent has been used to precipitate cadmium from dilute sulfuric acid in the presence of large amounts of zinc.<sup>150</sup> Antimony, arsenic, bismuth, copper, lead, mercury, and silver interfere.

*Triphenyltin Chloride.*—



**Solubility.**—Soluble in acetone, ether, and ethyl alcohol; insoluble in water.

**Reagent Solution.**—Dissolve 2 g. of the reagent in 100 ml. of 95% ethyl alcohol.

**Reactions.**—The reagent precipitates fluoride as insoluble triphenyltin fluoride.<sup>161</sup> Carbonate, phosphate, and silicic acid interfere, but moderate amounts of bromide, chloride, iodide, nitrate, and sulfate do not.

## INORGANIC PRECIPITANTS

Very few inorganic precipitants are specific in their action under any conditions, but some are sufficiently selective to permit their use in a number of important separations. For example, hydrochloric acid yields precipitates only with lead, mercury(I), silver, and thallium(I) ions, and sulfate ions precipitate only barium, lead, and strontium, and perhaps calcium. Further, some nonselective precipitants, such as ammonium hydroxide and hydrogen sulfide, which precipitate many ions, are still extremely useful for special group separations.

Improved separations using inorganic precipitants have been proposed in which masking reagents, such as EDTA, are used. The results of some of these studies are given in Table 5-4.

A selected list of common inorganic precipitants for the metals and anions is given in Table 5-5.

<sup>150</sup> Berg, R., and Roebeling, W., *Ber.*, 68, 403, 1935; Berg, R., *Angew. Chem.*, 23, 404, 1934; *Z. anal. Chem.*, 109, 305, 1937; 112, 161, 1938.

<sup>160</sup> Dwyer, F. P., and Gibson, N. A., *Analyst*, 75, 201, 1950.

<sup>161</sup> Allen, N., and Furman, N. H., *J. Am. Chem. Soc.*, 54, 4625, 1932.



TABLE 5-4. PRECIPITATION WITH INORGANIC REAGENTS  
IN THE PRESENCE OF EDTA <sup>162</sup>

<i>Reagent</i>	<i>Results</i>
Chloride	Silver and thallium precipitate from acetic acid solution. Mercury is reduced by EDTA and must be oxidized.
Iodide	Silver and thallium precipitate from acetic acid solution, but only silver precipitates from an ammoniacal solution.
Fluoride	In a solution of pH 4.0, lanthanum, rare earths, scandium, thorium, and yttrium precipitate. Calcium and magnesium do not.
Ammonium hydroxide	Antimony(III), beryllium, tin(IV), and titanium precipitate. Uranium is precipitated as ammonium diuranate.
Sodium hydroxide	Bismuth, hafnium, iron(III), niobium, tantalum, thorium, titanium, uranium, and zirconium precipitate.
Hydrogen sulfide	Antimony, arsenic, bismuth, mercury, silver, thallium, titanium precipitate immediately. Cadmium and copper precipitate slowly.
Chromate	Barium and thallium precipitate from an acetic acid solution.
Sulfate	In a solution of pH 4.0, only barium precipitates. Lead and strontium do not.
Tellurite	In a solution of pH 4.0, cesium, sodium, and tin(IV) precipitate. Potassium and rubidium do not.
Ferrocyanide	In a solution of pH 2.5, iron(II), manganese(II), silver, zinc, zirconium (and hafnium) precipitate.

<sup>162</sup> Pribil, R., Collection Czechoslov. Chem. Commun., 16, 542, 1951; Chem. Listy, 45, 57, 1951; Cheng, K. L., Anal. Chem., 33, 783, 1961.

TABLE 5-5. INORGANIC PRECIPITANTS  
THE METALS

	<i>Precipitated as</i>	<i>Precipitant</i>
Aluminum	Al(OH) <sub>3</sub> AlPO <sub>4</sub>	NH <sub>4</sub> OH, Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , NaNO <sub>2</sub> , KI + KIO <sub>3</sub> (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>
Ammonium	(NH <sub>4</sub> ) <sub>2</sub> PtCl <sub>6</sub>	H <sub>2</sub> PtCl <sub>6</sub>
Antimony	Sb <sub>2</sub> S <sub>3</sub>	H <sub>2</sub> S
Arsenic	As <sub>2</sub> S <sub>3</sub> MgNH <sub>4</sub> AsO <sub>4</sub> Ag <sub>3</sub> AsO <sub>4</sub>	H <sub>2</sub> S Magnesia mixture AgNO <sub>3</sub>
Beryllium	Be(OH) <sub>2</sub> BeNH <sub>4</sub> PO <sub>4</sub>	NH <sub>4</sub> OH, NH <sub>4</sub> NO <sub>2</sub> (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> + NH <sub>4</sub> NO <sub>3</sub>
Barium	BaSO <sub>4</sub> BaCrO <sub>4</sub> Ba(IO <sub>3</sub> ) <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub> K <sub>2</sub> CrO <sub>4</sub> KIO <sub>3</sub>

TABLE 5-5. (Continued)

## THE METALS

	<i>Precipitated as</i>	<i>Precipitant</i>
Bismuth	$(\text{BiO})_2\text{CO}_3$ $\text{BiOCl}$ $\text{BiOI}$ $\text{Bi}_2\text{S}_3$ $\text{BiPO}_4$	$(\text{NH}_4)_2\text{CO}_3$ $\text{HCl}$ $\text{KI}$ $\text{H}_2\text{S}, \text{Na}_2\text{S}_2\text{O}_3$ $(\text{NH}_4)_2\text{HPO}_4$
Cadmium	$\text{CdS}$ $\text{CdMoO}_4$ $\text{CdNH}_4\text{PO}_4$ $\text{Cd}_3[\text{Co}(\text{CN})_6]_2$	$\text{H}_2\text{S}$ $(\text{NH}_4)_2\text{MoO}_4$ $(\text{NH}_4)_2\text{HPO}_4$ $\text{K}_3[\text{Co}(\text{CN})_6]$
Calcium	$\text{CaWO}_4$ $\text{CaMoO}_4$ $\text{Ca}(\text{IO}_3)_2$ $\text{CaF}_2$	$\text{Na}_2\text{WO}_4$ $(\text{NH}_4)_2\text{MoO}_4$ $\text{HIO}_3$ $\text{KF}$
Cerium	$\text{CeO}_2$	$\text{H}_2\text{O}_2 + \text{NH}_4\text{OH}$
Cesium	$\text{Cs}_2\text{PtCl}_6$ $\text{Cs}_3[\text{Co}(\text{NO}_2)_6]$	$\text{H}_2\text{PtCl}_6$ $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$
Chromium	$\text{Cr}(\text{OH})_3$  $\text{CrPO}_4$ $\text{Hg}_2\text{CrO}_4$ $\text{Ag}_2\text{CrO}_4$ $\text{BaCrO}_4$ $\text{PbCrO}_4$	$\text{NH}_4\text{OH}, \text{KCNO}, \text{NH}_4\text{NO}_2, \text{KIO}_3$ $+ \text{KI}$ $(\text{NH}_4)_2\text{HPO}_4$ $\text{Hg}_2(\text{NO}_3)_2$ $\text{AgNO}_3$ $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$
Cobalt	$\text{CoS}$ $\text{CoNH}_4\text{PO}_4$ $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ $\text{Co}[\text{Hg}(\text{SCN})_4]$	$(\text{NH}_4)_2\text{S}$ $(\text{NH}_4)_2\text{HPO}_4$ $\text{KNO}_2$ $\text{K}_2[\text{Hg}(\text{SCN})_4]$
Copper	$\text{CuS}$ $\text{Cu}_2(\text{SCN})_2$ $\text{Cu}(\text{IO}_3)_2$ $\text{Cu}(\text{OH})_2$ $\text{Cu}$	$\text{H}_2\text{S}$ $\text{NH}_4\text{SCN} + \text{SO}_2$ $\text{KIO}_3$ $\text{NaOH}$ $\text{Al or Zn}$
Gallium	$\text{Ga}(\text{OH})_3$ $\text{Ga}_4[\text{Fe}(\text{CN})_6]_3$	$\text{NH}_4\text{OH}, \text{urea}$ $\text{K}_4[\text{Fe}(\text{CN})_6]$
Germanium	$\text{Mg}_2\text{GeO}_4$ $\text{GeS}_2$	$\text{MgSO}_4 + (\text{NH}_4)_2\text{SO}_4$ $\text{H}_2\text{S}$
Gold	$\text{Au}$	$\text{SO}_2, \text{FeSO}_4$
Indium	$\text{In}(\text{OH})_3$ $\text{In}_2\text{S}_3$ $\text{InPO}_4$	$\text{NH}_4\text{OH}, \text{NaOH}, \text{BaCO}_3, \text{KCNO}$ $\text{H}_2\text{S}$ $(\text{NH}_4)_2\text{HPO}_4$

TABLE 5-5. (Continued)

## THE METALS

	<i>Precipitated as</i>	<i>Precipitant</i>
Iron	$\text{Fe}(\text{OH})_3$ $\text{FePO}_4$ $\text{Fe}_3[\text{Co}(\text{CN})_6]_2$	$\text{NH}_4\text{OH}$ , $\text{NH}_4\text{NO}_2$ $(\text{NH}_4)_3\text{PO}_4$ $\text{K}_3[\text{Co}(\text{CN})_6]$
Lanthanum	$\text{La}(\text{OH})_3$	$\text{NH}_4\text{OH}$
Lead	$\text{PbS}$ $\text{PbSO}_4$ $\text{PbCrO}_4$ $\text{PbMoO}_4$ $\text{Pb}(\text{IO}_3)_2$ $\text{Pb}_3\text{H}_4(\text{IO}_6)_2$	$\text{H}_2\text{S}$ $\text{H}_2\text{SO}_4$ $\text{K}_2\text{CrO}_4$ $(\text{NH}_4)_2\text{MoO}_4$ $\text{KIO}_3$ $\text{KIO}_4$
Lithium	$\text{LiZn}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9$ $\text{Li}_3\text{PO}_4$ $\text{Li}_5\text{IO}_6$ (approx.) $\text{LiKFeIO}_6$	$\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ $\text{Na}_2\text{HPO}_4$ $\text{KIO}_4$ $\text{KIO}_4$
Magnesium	$\text{MgNH}_4\text{PO}_4$ $\text{MgNH}_4\text{AsO}_4$	Magnesia mixture $(\text{NH}_4)_3\text{AsO}_4 + \text{NH}_4\text{Cl}$
Manganese	$\text{MnO}_2$ $\text{MnNH}_4\text{PO}_4$ $\text{Mn}_3[\text{Co}(\text{CN})_6]$	$\text{KClO}_3 + \text{HNO}_3$ $(\text{NH}_4)_2\text{HPO}_4$ $\text{K}_3[\text{Co}(\text{CN})_6]$
Mercury	$\text{HgS}$ $\text{Hg}_2\text{Cl}_2$ $\text{Hg}$ $\text{Hg}[\text{Zn}(\text{SCN})_4]$ $\text{Hg}_5(\text{IO}_6)_2$ $\text{Hg}[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]_2$ $\text{Hg}_2(\text{IO}_3)_2$ $\text{Hg}(\text{IO}_3)_2$	$\text{H}_2\text{S}$ $\text{HCl}$ $\text{SnCl}_2$ $\text{ZnSO}_4 + \text{NH}_4\text{SCN}$ $\text{KIO}_4$ Reinecke's salt $\text{KIO}_3$ $\text{KIO}_3$
Molybdenum	$\text{PbMoO}_4$ $\text{MoS}_3$ $\text{Ag}_2\text{MoO}_4$	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ $\text{H}_2\text{S}$ $\text{AgNO}_3$
Nickel	$\text{NiS}$ $\text{Ni}(\text{OH})_2$ $\text{Ni}_3[\text{Co}(\text{CN})_6]_2$	$(\text{NH}_4)_2\text{S}$ , $\text{Na}_2\text{S}_2\text{O}_3$ $\text{NaOH}$ $\text{K}_3[\text{Co}(\text{CN})_6]$
Palladium	$\text{Pd}$ $\text{PdI}$ $\text{PdS}$ $\text{Pd}(\text{CN})_2$	$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ $\text{KI}$ $\text{H}_2\text{S}$ $\text{Hg}(\text{CN})_2$
Platinum	$(\text{NH}_4)_2\text{PtCl}_6$	$\text{NH}_4\text{Cl}$

TABLE 5-5. (Continued)

## THE METALS

	<i>Precipitated as</i>	<i>Precipitant</i>
Potassium	$K_2PtCl_6$ $KClO_4$ $K_2Na[Co(NO_2)_6]$ $KIO_4$	$H_2PtCl_6$ $HClO_4$ $Na_3[Co(NO_2)_6]$ $HIO_4$
Rhenium	$Re_2S_7$	$H_2S$
Rubidium	$(Rb, Na)_3[Co(NO_2)_6]$ $Rb_2PtCl_6$	$Na_3[Co(NO_2)_6]$ $H_2PtCl_6$
Scandium	$Sc(OH)_3$ $ScF_3$	$NH_4OH$ $Na_2SiF_6$
Selenium	$Se$	$Na_2SO_3$ , $SO_2$ , $SnCl_2$ , $N_2H_4$
Silver	$AgCl$ $Ag_3[Co(CN)_6]$	$HCl$ $K_3[Co(CN)_6]$
Sodium	$NaZn(UO_2)_3(C_2H_3O_2)_9 \cdot 6H_2O$ $Na_6Cs_3[Bi(NO_2)_6]_5$	$UO_2(C_2H_3O_2)_2 + Zn(C_2H_3O_2)_2$ $KNO_2 + Bi(NO_3)_3 + CsNO_3$
Strontium	$SrSO_4$ $SrF_2$ $Sr(IO_3)_2$	$H_2SO_4$ $KF$ $HIO_3$
Tellurium	$Te$	$N_2H_4$ , $H_3PO_2$ , $SO_2$
Thallium	$Tl_2CrO_4$ $Tl_3[Co(NO_2)_6]$ $TlI$	$K_2CrO_4$ $Na_3[Co(NO_2)_6]$ $KI$
Thorium	$Th(IO_3)_4$ $ThF_4$ $Th(OH)_4$	$KIO_3$ $NH_4F$ $NH_4OH$
Tin	$Sn(OH)_4$ $SnS_2$ $H_2SnO_3$	$NH_4OH$ $H_2S$ $HNO_3$
Titanium	$H_2[TiO_2, SeO_3] \cdot 2H_2O$ $Ti(OH)_4$ $Ti(IO_3)_4 \cdot 3KIO_3$	$H_2SeO_3$ $NaOH$ , $NH_4OH$ $KIO_3$
Tungsten	$BaWO_4$	$BaCl_2$
Uranium	$(NH_4)_2U_2O_7$ $UO_4 \cdot 2H_2O$	$NH_4OH$ $H_2O_2$
Vanadium	$(Hg_2)_3(VO_4)_2$ $Ag_3VO_4$ $Pb_3(VO_4)_2$	$Hg_2(NO_3)_2$ $AgNO_3$ $Pb(C_2H_3O_2)_2$

TABLE 5-5. (Continued)

## THE METALS

	<i>Precipitated as</i>	<i>Precipitant</i>
Zinc	$\text{ZnNH}_4\text{PO}_4$	$(\text{NH}_4)_2\text{HPO}_4$
	$\text{ZnS}$	$\text{H}_2\text{S}$
	$\text{Zn}[\text{Hg}(\text{SCN})_4]$	$\text{K}_2[\text{Hg}(\text{SCN})_4]$
	$\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$	$\text{K}_4[\text{Fe}(\text{CN})_6]$
Zirconium	$\text{ZrH}_2(\text{PO}_4)_2$	$(\text{NH}_4)_2\text{HPO}_4$
	$\text{ZrOSeO}_3$	$\text{H}_2\text{SeO}_3$
	$\text{ZrOHAsO}_4$	$\text{Na}_2\text{HAsO}_4$

## THE ANIONS

	<i>Precipitated as</i>	<i>Precipitant</i>
Borate	$\text{Ca}(\text{BO}_2)_2$	$\text{CaCl}_2$
	$\text{Ba}(\text{BO}_2)_2$	$\text{BaCl}_2$
Bromide	$\text{AgBr}$	$\text{AgNO}_3$
Chloride	$\text{AgCl}$	$\text{AgNO}_3$
Chromate	See Chromium	
Cyanide	$\text{AgCN}$	$\text{AgNO}_3$
Ferriocyanide	$\text{Ag}_3[\text{Fe}(\text{CN})_6]$	$\text{AgNO}_3$
	$[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{CN})_6]$	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
Ferrocyanide	$\text{Ag}_4[\text{Fe}(\text{CN})_6]$	$\text{AgNO}_3$
Fluoborate	$\text{KBF}_4$	$\text{KCl}$
Fluoride	$\text{CaF}_2$	$\text{CaCl}_2$
	$\text{PbClF}$	$\text{HCl} + \text{Pb}(\text{NO}_3)_2$
	$\text{ThF}_4$	$\text{Th}(\text{NO}_3)_4$
Iodide	$\text{AgI}$	$\text{AgNO}_3$
	$\text{PdI}_2$	$\text{PdCl}_2$
	$\text{PbI}_2$	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$
Molybdate	See Molybdenum	
Perchlorate	$\text{KClO}_4$	$\text{KC}_2\text{H}_3\text{O}_2$
Phosphate	$(\text{ZrO})\text{HPO}_4$	$\text{ZrCl}_4$
	$(\text{NH}_4)_3(\text{MoO}_3)_{12}\text{PO}_4$	$(\text{NH}_4)_2\text{MoO}_4 + \text{HNO}_3$
	$\text{MgNH}_4\text{PO}_4$	Magnesia mixture
Silicate	$\text{SiO}_2$	$\text{HCl}$
Sulfate	$\text{BaSO}_4$	$\text{BaCl}_2$
	$[\text{Co}(\text{NH}_3)_6]\text{BrSO}_4$	$[\text{Co}(\text{NH}_3)_6]\text{Br}_3$

TABLE 5-5. (Continued)

## THE ANIONS

	<i>Precipitated as</i>	<i>Precipitant</i>
Thiocyanate	AgSCN $\text{Cu}_2(\text{SCN})_2$	$\text{AgNO}_3$ $\text{CuSO}_4 + \text{SO}_2$
Tungstate	See Tungsten	
Vanadate	See Vanadium	

# GENERATION OF REAGENTS IN HOMOGENEOUS PHASE

By

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The modern concept of precipitation from homogeneous solution was introduced in 1937 by Willard and Tang.<sup>163</sup> In this technique, the precipitating agent is generated throughout the solution by a homogeneous chemical reaction. Because the reagent is not added directly and thus undesirable concentration effects are avoided, the precipitate formed is dense, readily filterable, and most important, exhibits minimal coprecipitation.

The following procedure is given as an illustrative example of the technique of precipitation from homogeneous solution. This is a procedure for the determination of nickel with dimethylglyoxime generated *in situ* from biacetyl and hydroxylamine.

Adjust the pH of the solution containing no more than 200 mg. of nickel to  $7.5 \pm 0.1$  with ammonium hydroxide. Add a quantity of biacetyl equal to six times the approximate weight of nickel to be precipitated, but never less than 0.12 g. in any case. Next add with stirring, 50 ml. of a solution, adjusted to pH  $7.5 \pm 0.1$  with ammonium hydroxide, containing a quantity of hydroxylamine hydrochloride equal to four times the weight of biacetyl added, but in no case less than 0.5 g. Adjust the final volume of the solution to 100 ml. if 0.5 to 5 mg. of nickel are present, to 200 ml. for 5 to 50 mg., to 300 ml. for 50 to 100 mg., or to 400 ml. for 100 to 200 mg. Allow the solution to stand at room temperature for at least one hour (or longer) after precipitation begins and then heat to 80 to 90°C. for two hours. Cool the solution, filter, wash the precipitate with water, and dry to constant weight at 140°C.

Similarly, many ions can be generated at a slow rate so that precipitates with vastly improved characteristics are formed. The reactions, elements precipitated, diverse ions studied, and pertinent references will be presented in the following paragraphs in outline form; fractional precipitation methods will be omitted. For a comprehensive treatment of the entire subject of precipitation from homogeneous solution, see Gordon, Salutsky, and Willard.<sup>164</sup>

## HYDROXIDES AND BASIC SALTS

### *Hydrolysis of Urea to Raise the pH of the Solution.*

Reaction.



<sup>163</sup> Willard, H. H., and Tang, N. K., J. Am. Chem. Soc., 59, 1190, 1937.

<sup>164</sup> Gordon, L., Salutsky, M. L., and Willard, H. H., Precipitation from Homogeneous Solution, John Wiley and Sons, Inc., New York, 1959.

## Elements Precipitated.

- (a) Aluminum (as the basic succinate).
- <sup>165, 166</sup>

Quantity Precipitated. 1 to 100 mg.

Diverse Ions Studied. Ba, Ca, Cd, Co, Cu, Fe, Mg, Mn, Ni, Zn, and phosphate.

- (b) Aluminum (as the basic sulfate).
- <sup>163, 165</sup>

Quantity Precipitated. 100 mg.

Diverse Ions Studied. Ca, Cd, Co, Cu, Mg, Mn, Ni, and Zn.

- (c) Bismuth (as the basic formate).
- <sup>167</sup>

Quantity Precipitated. 100 to 500 mg.

Diverse Ions Studied. Pb.

- (d) Gallium (as the basic sulfate).
- <sup>168, 169, 170</sup>

Quantity Precipitated. 10 to 130 mg.

Diverse Ions Studied. Ca, Mn, and Zn.

- (e) Iron (as the basic formate).
- <sup>171, 172</sup>

Quantity Precipitated. 20 to 670 mg.

Diverse Ions Studied. Ba, Ca, Co, Cd, Cu, Mg, Mn, and Zn.

- (f) Thorium (as the basic formate or sulfate).
- <sup>173, 174</sup>

Quantity Precipitated. 50 to 100 mg.

Diverse Ions Studied. Ce, Gd, La, Nd, Pr, and Y.

- (g) Tin (as the basic sulfate).
- <sup>172, 175, 176</sup>

Quantity Precipitated. 150 to 300 mg.

Diverse Ions Studied. Fe, Mn, and Ni.

- (h) Zirconium (as the basic formate or succinate).
- <sup>173</sup>

Quantity Precipitated. 100 mg.

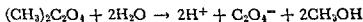
Diverse Ions Studied. Th.

## OXALATES

*Hydrolysis of Esters to Produce Oxalate Ion.*

## Dimethyl Oxalate.

## Reaction.



## Elements Precipitated.

- (a) Actinium.
- <sup>177</sup>

Quantity Precipitated. 25 to 40 mg.

Diverse Ions Studied. Al, Fe.

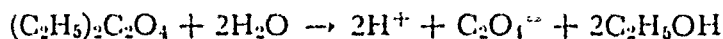
<sup>165</sup> Willard, H. H., and Tang, N. K., *Ind. Eng. Chem., Anal. Ed.*, **9**, 357, 1937.<sup>166</sup> Gordon, L., unpublished research.<sup>167</sup> Cartwright, P. F. S., *Analyst*, **85**, 216, 1960.<sup>168</sup> Willard, H. H., and Fogg, H. C., *J. Am. Chem. Soc.*, **59**, 1197, 1937.<sup>169</sup> Willard, H. H., and Fogg, H. C., *J. Am. Chem. Soc.*, **59**, 2422, 1937.<sup>170</sup> Willard, H. H., and Fogg, H. C., *J. Am. Chem. Soc.*, **59**, 40, 1937.<sup>171</sup> Willard, H. H., and Sheldon, J. L., *Anal. Chem.*, **22**, 1162, 1950.<sup>172</sup> Sheldon, J. L., Ph.D. dissertation, University of Michigan, 1940.<sup>173</sup> Gordon, L., Ph.D. dissertation, University of Michigan, 1947.<sup>174</sup> Willard, H. H., and Gordon, L., *Anal. Chem.*, **20**, 165, 1948.<sup>175</sup> Willard, H. H., and Gordon, L., *Anal. Chem.*, **25**, 170, 1953.<sup>176</sup> Gordon, L., Teicher, H., and Burt, B. P., *Anal. Chem.*, **26**, 992, 1954.<sup>177</sup> Salutsky, M. L., and Kirby, H. W., *Anal. Chem.*, **28**, 1781, 1956.



- (b) Americium.<sup>178</sup>  
 Quantity Precipitated. Not given.  
 Diverse Ions Studied. La.
- (c) Calcium.<sup>179, 180</sup>  
 Quantity Precipitated. 1 to 125 mg.  
 Diverse Ions Studied. Ba, Mg.
- (d) Rare Earths.<sup>181, 182</sup>  
 Quantity Precipitated. 50 to 200 mg.  
 Diverse Ions Studied. Rare earths, Ca, Th, and Y.
- (e) Thorium.<sup>174, 182, 183, 184, 185</sup>  
 Quantity Precipitated. 30 to 200 mg.  
 Diverse Ions Studied. Rare earths, Al, Ca, Ti, Zr, and phosphate.
- (f) Uranium.<sup>186</sup>  
 Quantity Precipitated. 10 mg.  
 Diverse Ions Studied. Ce, Sc.

Diethyl Oxalate.

Reaction.

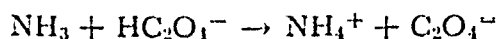


Elements Precipitated.

- (a) Magnesium.<sup>187</sup>  
 Quantity Precipitated. 1 to 100 mg.  
 Diverse Ions Studied. Li, Na, chloride, perchlorate, and sulfate.
- (b) Zinc.<sup>188, 189</sup>  
 Quantity Precipitated. 1 to 50 mg.  
 Diverse Ions Studied. Ca, Cd, Cu, Fe, Mg, Pb, acetate, chloride, and sulfate.

*Hydrolysis of Urea to Raise the pH of an Acid Solution Containing the Bioxalate Ion.*

Reactions.



Element Precipitated.

Calcium.<sup>190, 191</sup>

- Quantity Precipitated. 0.5 to 300 mg.  
 Diverse Ions Studied. Al, Cr, Fe, Mg, Mn, Ti, chloride, phosphate, and sulfate.

*Hydrolysis of Acetone Dioxalic Acid.*

<sup>178</sup> Hermann, J. A., Ph.D. dissertation, University of New Mexico, 1955.

<sup>179</sup> Gordon, L., and Wroczyński, A. F., Anal. Chem., 24, 896, 1952.

<sup>180</sup> Litvin, K. I., Anal. Abstr., 5, 3633, 1958.

<sup>181</sup> Feibush, A. M., Rowley, K., and Gordon, L., Anal. Chem., 30, 1605, 1958.

<sup>182</sup> Carron, M. K., Skinner, D. L., and Stevens, R. E., Anal. Chem., 27, 1058, 1955.

<sup>183</sup> Kall, H. L., and Gordon, L., Anal. Chem., 25, 1256, 1953.

<sup>184</sup> Gordon, L., Vanselow, C. H., and Willard, H. H., Anal. Chem., 21, 1323, 1949.

<sup>185</sup> Banks, C. V., and Edwards, R. E., Anal. Chem., 27, 947, 1955.

<sup>186</sup> Block, J., and Gordon, L., unpublished research.

<sup>187</sup> Gordon, L., and Caley, E. R., Anal. Chem., 20, 560, 1948.

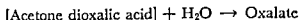
<sup>188</sup> Caley, E. R., Gordon, L., and Simmons, E. A., Jr., Anal. Chem., 22, 1060, 1950.

<sup>189</sup> Vance, J. E., and Borup, R. E., Anal. Chem., 25, 610, 1953.

<sup>190</sup> Chan, F. L., Ph.D. dissertation, University of Michigan, 1932.

<sup>191</sup> Ingols, R. S., and Murray, P. E., Anal. Chem., 21, 525, 1949.

Reaction.



Element Precipitated.

Thorium.<sup>192</sup>

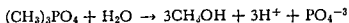
Quantity Precipitated. Not given.

Diverse Ions Studied. Rare earths, Ti, and Zr.

## PHOSPHATES

*Hydrolysis of Trimethyl Phosphate to Produce Phosphate Ion.*

Reaction.



Element Precipitated.

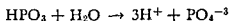
Zirconium.<sup>193</sup>

Quantity Precipitated. 2 to 160 mg.

Diverse Ions Studied. Al, As, B, Bi, Ca, Cd, Ce, Co, Cr, Cu, Fe, Hg, Mg, Mn, Na, Ni, K, Sb, Sn, Th, U, V, Zn, and tartrate.

*Hydrolysis of Metaphosphoric Acid to Produce Phosphate Ion.*

Reaction.



Element Precipitated.

Zirconium.<sup>193</sup>

Quantity Precipitated. 0.2 to 150 mg.

Diverse Ions Studied. Al, As, B, Bi, Cd, Ce, Co, Cr, Cu, Fe, Hg, Mg, Mn, Na, Ni, K, Sb, Sn, Th, V, Y, Zn, perchlorate, and tartrate.

*Hydrolysis of Phosphorus Oxychloride to Produce Phosphate Ion.*

Reaction.



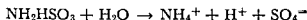
Element Precipitated.

Magnesium.<sup>190, 194</sup>

## SULFATES

*Hydrolysis of Sulfamic Acid to Produce Sulfate Ion.*

Reaction.



Elements Precipitated.

(a) Barium.<sup>195, 196, 197</sup>

Quantity Precipitated. 1 to 170 mg.

<sup>192</sup> Zaikovskii, F. V., and Gerkhard, L. I., Nuc. Sci. Abstr., 13, 1177, 1959.

<sup>193</sup> Willard, H. H., and Hahn, R. B., Anal. Chem., 21, 293, 1949.

<sup>194</sup> No information available as to either quantity precipitated or diverse ions studied.

<sup>195</sup> Freund, H., Ph.D. dissertation, University of Michigan, 1945.

<sup>196</sup> Wagner, W. F., and Wuellner, J. A., Anal. Chem., 24, 1031, 1952.

<sup>197</sup> Gordon, L., and Rowley, L., Anal. Chem., 29, 34, 1957.

Diverse Ions Studied. Ca, Fe, Ra, Sr, nitrate, and phosphate.

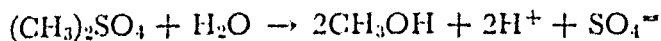
(b) Lead.<sup>198, 199</sup>

Quantity Precipitated.

Diverse Ions Studied. Constituents in NBS alloys and bar lead.

*Hydrolysis of Dimethyl Sulfate to Produce Sulfate Ion.*

Reaction.



Elements Precipitated.

(a) Barium.<sup>200</sup>

Quantity Precipitated. 1 to 100 mg.

Diverse Ions Studied. Al, Ca, Fe, K, Mg, Na, and Sr.

(b) Calcium.<sup>200</sup>

Quantity Precipitated. 50 to 100 mg.

Diverse Ions Studied. Al, Fe, K, Mg, and Na.

(c) Lead.<sup>201</sup>

Quantity Precipitated. 1 to 100 mg.

Diverse Ions Studied. Al, Cu, Fe, Mn, Ni, Zn, and nitrate.

(d) Strontium.<sup>200</sup>

Quantity Precipitated. 1 to 125 mg.

Diverse Ions Studied. Al, Ca, Fe, K, Mg, and Na.

*Hydrolysis of Potassium Methyl Sulfate to Produce Sulfate Ion.*

Reaction.



Element Precipitated.

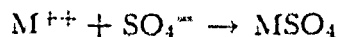
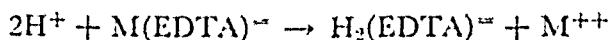
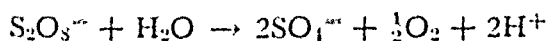
Barium.<sup>173</sup>

Quantity Precipitated. Not given.

Diverse Ions Studied. None.

*Destruction of EDTA Complex to Release Cation in the Presence of Sulfate Ion.*

Reaction.



Element Precipitated.

Barium.<sup>202</sup>

Quantity Precipitated. 10 to 200 mg.

Diverse Ions Studied. Ca, Fe, K, Na, and Sr.

## SULFIDES

*Hydrolysis of Thioamides to Produce Sulfide Ion.*

Thioacetamide.

<sup>198</sup> Jarnagin, R. C., and Kenner, C. T., Anal. Chem., 24, 2016, 1952.

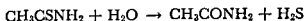
<sup>199</sup> Kenner, C. T., private communication.

<sup>200</sup> Elving, P. J., and Van Atta, R. D., Anal. Chem., 22, 1375, 1950.

<sup>201</sup> Elving, P. J., and Zook, W. C., Anal. Chem., 25, 502, 1953.

<sup>202</sup> Heyn, A. H. A., and Schupak, E., Anal. Chem., 26, 1243, 1954.

Reaction.

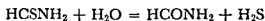


Elements Precipitated.

- (a) Antimony.<sup>203</sup>  
Quantity Precipitated. 5 to 350 mg.  
Diverse Ions Studied. None.
- (b) Arsenic.<sup>204</sup>  
Quantity Precipitated. 10 to 150 mg.  
Diverse Ions Studied. None.
- (c) Bismuth.<sup>205</sup>  
Quantity Precipitated. 15 to 280 mg.  
Diverse Ions Studied. None.
- (d) Cadmium.<sup>206</sup>  
Quantity Precipitated. 15 to 150 mg.  
Diverse Ions Studied. None.
- (e) Copper.<sup>207, 208</sup>  
Quantity Precipitated. 15 to 300 mg.  
Diverse Ions Studied. Ni, Zn.
- (f) Lead.<sup>209</sup>  
Quantity Precipitated. 10 to 250 mg.  
Diverse Ions Studied. None.
- (g) Manganese.<sup>210</sup>  
Quantity Precipitated. 5 to 115 mg.  
Diverse Ions Studied. Ca, Mg.
- (h) Mercury.<sup>211</sup>  
Quantity Precipitated. 20 to 450 mg.  
Diverse Ions Studied. None.
- (i) Molybdenum.<sup>212, 213</sup>  
Quantity Precipitated. 10 to 165 mg.  
Diverse Ions Studied. Al, Ce, Nd, Ti, and W.
- (j) Tin.<sup>214</sup>  
Quantity Precipitated. 12 to 180 mg.  
Diverse Ions Studied. None.

Thioformamide.

Reaction.



<sup>203</sup> Flaschka, H., and Jakobljovich, H., Anal. Chim. Acta, 4, 247, 1950.

<sup>204</sup> Flaschka, H., and Jakobljovich, H., Anal. Chim. Acta, 4, 486, 1950.

<sup>205</sup> Flaschka, H., and Jakobljovich, H., Anal. Chim. Acta, 4, 351, 1950.

<sup>206</sup> Flaschka, H., and Jakobljovich, H., Anal. Chim. Acta, 4, 602, 1950.

<sup>207</sup> Flaschka, H., and Jakobljovich, H., Anal. Chim. Acta, 4, 482, 1950.

<sup>208</sup> Krijn, G. C., Chem. Abstr., 53, 3997f, 1959.

<sup>209</sup> Flaschka, H., and Jakobljovich, H., Anal. Chim. Acta, 4, 606, 1950.

<sup>210</sup> Flaschka, H., and Abdine, H., Chemist Analyst, 44, 8, 1855.

<sup>211</sup> Flaschka, H., and Jakobljovich, H., Anal. Chim. Acta, 5, 152, 1951.

<sup>212</sup> Flaschka, H., and Jakobljovich, H., Anal. Chim. Acta, 4, 356, 1950.

<sup>213</sup> McNerney, W. N., and Wagner, W. F., Anal. Chem., 29, 1177, 1957.

<sup>214</sup> Flaschka, H., and Jakobljovich, H., Anal. Chim. Acta, 5, 60, 1951.

## Elements Precipitated.

- (a) Antimony.<sup>215</sup>  
Quantity Precipitated. 10 to 315 mg.  
Diverse Ions Studied. As, Sn.
- (b) Arsenic.<sup>215, 216, 217</sup>  
Quantity Precipitated. 20 to 350 mg.  
Diverse Ions Studied. Cu, Sb, and Sn.
- (c) Copper.<sup>217, 218</sup>  
Quantity Precipitated. 15 to 260 mg.  
Diverse Ions Studied. As.
- (d) Iridium.<sup>219</sup>  
Quantity Precipitated. 20 to 60 mg.  
Diverse Ions Studied. Pd.
- (e) Palladium.<sup>219, 220</sup>  
Quantity Precipitated. 30 to 250 mg.  
Diverse Ions Studied. Ir.
- (f) Platinum.<sup>221</sup>  
Quantity Precipitated. 16 to 100 mg.  
Diverse Ions Studied. None.
- (g) Rhodium.<sup>219</sup>  
Quantity Precipitated. 25 mg.  
Diverse Ions Studied. None.
- (h) Tin.<sup>215</sup>  
Quantity Precipitated. 15 to 350 mg.  
Diverse Ions Studied. As, Sb.

 Hydrolysis of Trithiocarbonic Acid to Produce Sulfide Ion.  
Reaction.


## Elements Precipitated.

- (a) Antimony.<sup>222</sup>  
Quantity Precipitated. 120 to 175 mg.  
Diverse Ions Studied. None.
- (b) Copper.<sup>223</sup>  
Quantity Precipitated. 15 to 235 mg.  
Diverse Ions Studied. None.
- (c) Iron.<sup>224, 225</sup>  
Quantity Precipitated. 10 to 230 mg.  
Diverse Ions Studied. Al, Ti, and Zn.

<sup>215</sup> Musil, A., Gagliardi, E., and Reischl, K., Z. anal. Chem., 140, 342, 1953.

<sup>216</sup> Gagliardi, E., and Loidl, E., Z. anal. Chem., 132, 33, 1951.

<sup>217</sup> Gagliardi, E., and Loidl, E., Z. anal. Chem., 132, 274, 1951.

<sup>218</sup> Gagliardi, E., and Loidl, E., Z. anal. Chem., 132, 87, 1951.

<sup>219</sup> Gagliardi, E., and Pietsch, R., Monatsh., 83, 487, 1952.

<sup>220</sup> Gagliardi, E., and Pietsch, R., Monatsh., 82, 432, 1951.

<sup>221</sup> Gagliardi, E., and Pietsch, R., Monatsh., 82, 656, 1951.

<sup>222</sup> Gagliardi, E., and Pilz, W., Z. anal. Chem., 136, 344, 1952.

<sup>223</sup> Gagliardi, E., and Pilz, W., Monatsh., 83, 54, 1952.

<sup>224</sup> Pilz, W., Monatsh., 84, 471, 1953.

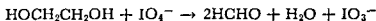
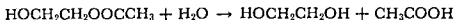
<sup>225</sup> Musil, A., and Pilz, W., Z. anal. Chem., 141, 19, 1953.

- (d) Manganese.<sup>225, 226</sup>  
 Quantity Precipitated. 10 to 210 mg.  
 Diverse Ions Studied. Ca, Mg, and Zn.
- (e) Molybdenum.<sup>227</sup>  
 Quantity Precipitated. 50 to 210 mg.  
 Diverse Ions Studied. None.
- (f) Zinc.<sup>225, 228</sup>  
 Quantity Precipitated. 20 to 240 mg.  
 Diverse Ions Studied. Fe, Mg, and Mn.

### OTHER METHODS OF PRECIPITATION FROM HOMOGENEOUS SOLUTION

#### *Precipitation of Iodates.*

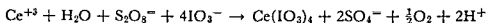
Hydrolysis of  $\beta$ -Hydroxyethyl Acetate and Subsequent Reaction with Periodate.  
 Reaction.



Elements Precipitated.

- (a) Iron.<sup>229</sup>  
 Quantity Precipitated. Not given.  
 Diverse Ions Studied. None.
- (b) Thorium.<sup>230</sup>  
 Quantity Precipitated. 1 to 150 mg.  
 Diverse Ions Studied. Fe, Mn, rare earths, Sn, Ti, and phosphate.
- (c) Zirconium.<sup>230</sup>  
 Quantity Precipitated. Not given.  
 Diverse Ions Studied. None.

Oxidation of Ce(III) to Ce(IV) in the Presence of Iodate.<sup>231, 232</sup>  
 Reaction.

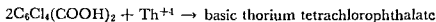


Quantity Precipitated. 20 to 80 mg. of cerium.

Diverse Ions Studied. Er, Gd, La, Nd, Pr, Sc, Sm, and Y.

#### *Precipitation of Thorium Tetrachlorophthalate.*<sup>233</sup>

Reaction.



Quantity Precipitated. 1 to 100 mg. of thorium.

Diverse Ions Studied. Ce, La, Nd, Pr, and Y.

<sup>226</sup> Pilz, W., *Monatsh.*, 83, 1291, 1952.

<sup>227</sup> Gagliardi, L., and Pilz, W., *Z. anal. Chem.*, 136, 103, 1952.

<sup>228</sup> Pilz, W., *Monatsh.*, 83, 471, 1952.

<sup>229</sup> Ginsburg, L., Ph.D. dissertation, Syracuse University, 1955.

<sup>230</sup> Stine, C. R., and Gordon, L., *Anal. Chem.*, 25, 1519, 1953.

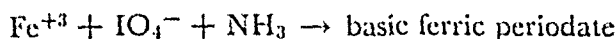
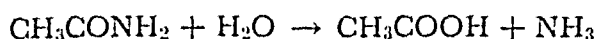
<sup>231</sup> Willard, H. H., and Yu, S. T., *Anal. Chem.*, 25, 1754, 1953.

<sup>232</sup> Kimura, K., Natsume, H., and Suzuki, Y., *Anal. Abstr.*, 5, 2922, 1958.

<sup>233</sup> Gordon, L., Vanselow, C. H., and Willard, H. H., *Anal. Chem.*, 21, 1323, 1949.

*Precipitation of Iron(III) Periodate.*<sup>234, 235</sup>

Reaction.

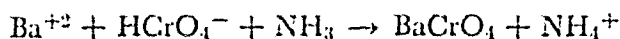


Quantity Precipitated. 5 to 85 mg. of iron.

Diverse Ions Studied. Al, Y, and Zn.

*Precipitation of Barium Chromate.*<sup>236</sup>

Reaction.



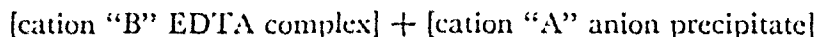
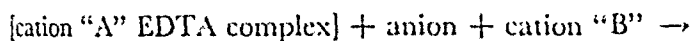
Quantity Precipitated. 100 mg. of barium.

Diverse Ions Studied. Ca, Sr.

*Precipitation from EDTA Solutions.*

Precipitation by Replacement Technique.

Reaction.



Elements Precipitated.

(a) Barium (as chromate).<sup>237</sup>

Quantity Precipitated. 70 mg.

Diverse Ions Studied. Ca, Fe, Pb, and Sr.

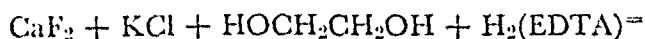
(b) Barium (as sulfate).<sup>238, 239</sup>

(c) Thorium (as oxalate).<sup>238, 239</sup>

(d) Yttrium (as oxalate).<sup>238, 239</sup>

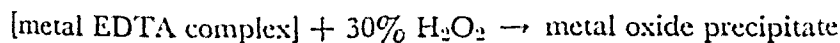
Precipitation of Calcium Fluoride.<sup>238, 240</sup>

Reaction.



*Precipitation of Hydrous Metal Oxides.*

Reaction.



Elements Precipitated.

(a) Iron.<sup>241</sup>

Quantity Precipitated. 70 mg.

Diverse Ions Studied. None.

<sup>234</sup> Gordon, L., and Ginsburg, L., *Anal. Chem.*, **29**, 38, 1957.

<sup>235</sup> Ginsburg, L., Milar, K., and Gordon, L., *Anal. Chem.*, **29**, 46, 1957.

<sup>236</sup> Gordon, L., and Firsching, F. H., *Anal. Chem.*, **26**, 759, 1954.

<sup>237</sup> Firsching, F. H., *Talanta*, **2**, 326, 1959.

<sup>238</sup> No information available as to either quantity precipitated or diverse ions studied.

<sup>239</sup> Firsching, F. H., Ph.D. dissertation, Syracuse University, 1954.

<sup>240</sup> Shaver, K. J., and Gordon, L., unpublished research.

<sup>241</sup> MacNevin, W. M., and Dunton, M. L., *Anal. Chem.*, **26**, 1247, 1954.

(b) Thorium.<sup>242</sup>

Quantity Precipitated. Not given.

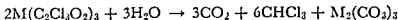
Diverse Ions Studied. Rare earths.

Precipitation of Rare Earth Oxalates.<sup>238, 243</sup>

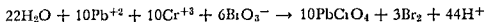
Reaction.

rare earth oxalates in hot EDTA solution  $\xrightarrow{\text{cooling}}$   
fractionally precipitated rare earth oxalates

*Precipitation of Rare Earth Carbonates by Trichloroacetate Hydrolysis.*<sup>238, 244</sup>  
Reaction.



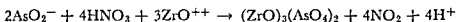
*Precipitation of Lead Chromate by Oxidation of Chromium(III).*<sup>245</sup>  
Reaction.



Quantity Precipitated. 790 to 950 mg. of lead.

Diverse Ions Studied. Constituents in steel.

*Precipitation of Zirconium Arsenate by Oxidation of Arsenite.*<sup>246</sup>  
Reaction.



Quantity Precipitated. 2 to 25 mg. of zirconium.

Diverse Ions Studied. None.

*Precipitation by Synthesis of Organic Chelate Reagents.*

Azimidobenzene.

Reaction.

metal ion +  $\text{NaNO}_2$  + o-phenylenediamine  $\xrightarrow{\text{acetic acid}}$  metal azimidobenzene chelate

(a) Copper.<sup>247</sup>

Quantity Precipitated. Not given.

Diverse Ions Studied. Cd.

(b) Silver.<sup>247</sup>

Quantity Precipitated. Not given.

Diverse Ions Studied. Cd.

*1-Nitroso-2-naphthol.*<sup>248</sup>

Reaction.

$\text{Co}^{+3} + 2\text{-Naphthol} + \text{NaNO}_2 \xrightarrow{\text{controlled pH}}$  cobalt 1-Nitroso-2-naphthol chelate

<sup>242</sup> Gordon, L., unpublished research.

<sup>243</sup> Gordon, L., and Shaver, K. J., *Anal. Chem.*, **25**, 784, 1953.

<sup>244</sup> Quill, L. L., and Salutsky, M. L., *J. Am. Chem. Soc.*, **72**, 3306, 1950.

<sup>245</sup> Hoffman, W. A., and Brandt, W. W., *Anal. Chem.*, **28**, 1487, 1956.

<sup>246</sup> Gump, J. R., and Sherwood, G. R., *Anal. Chem.*, **22**, 496, 1950.

<sup>247</sup> Tarasevich, N. I., *Chem. Abstr.*, **50**, 7652i, 1956.

<sup>248</sup> Brauner, P. A., and Heyn, A. H. A., private communication.

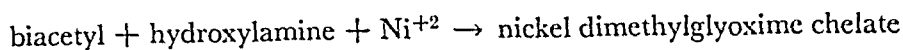


Quantity Precipitated. 10 to 100 mg. of cobalt.

Diverse Ions Studied. Fe, W.

Dimethylglyoxime.<sup>249</sup>

Reaction.

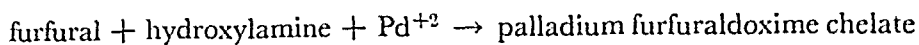


Quantity Precipitated. 0.5 to 200 mg. of nickel.

Diverse Ions Studied. Co, Cu, and Fe.

Furfuraldoxime.<sup>250</sup>

Reaction.

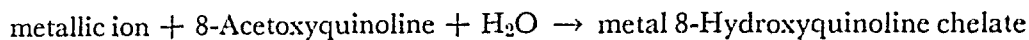


Quantity Precipitated. 20 to 70 mg. of palladium.

Diverse Ions Studied. Au, Cd, Ce, Co, Cr, Cu, Fe, Hg, Mo, Ni, Pt, V, and Zn.

8-Hydroxyquinoline.

Reaction.



Element Precipitated.

Thorium.<sup>251, 252</sup>

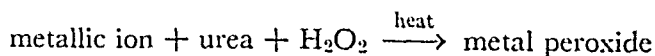
Quantity Precipitated. 1 to 140 mg.

Diverse Ions Studied. Ce.

NOTE: Aluminum, cadmium, cobalt, copper, iron, lead, magnesium, manganese, nickel, uranium, and zinc can also be precipitated with 8-acetoxyquinoline as indicated by preliminary experiments.<sup>251</sup>

Precipitation of Metals as Peroxides.

Reaction.



(a) Thorium.<sup>238, 253</sup>

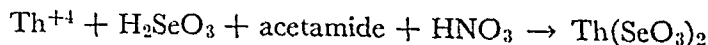
(b) Zirconium.<sup>253</sup>

Quantity Precipitated. 12,000 mg.

Diverse Ions Studied. None.

Precipitation of Thorium Selenite.<sup>254</sup>

Reaction.



Quantity Precipitated. Not given.

Diverse Ions Studied. Rare earths.

<sup>249</sup> Salesin, E. D., and Gordon, L., *Talanta*, 5, 81, 1960.

<sup>250</sup> Conejero, L. M., *Anal. Abstr.*, 6, 1756, 1959.

<sup>251</sup> Salesin, E. D., and Gordon, L., *Talanta*, 4, 75, 1960.

<sup>252</sup> Takiyama, K., Salesin, E. D., and Gordon, L., *Talanta*, 5, 231-7, 1960.

<sup>253</sup> Gantz, D. E., and Lambert, J. L., *J. Phys. Chem.*, 61, 112, 1957.

<sup>254</sup> Jen-Yin, Y., Kuang-Hua, D., and Feng-Chiao, H., *Chem. Abstr.*, 53, 8937f., 1959.

# MASKING AND DEMASKING

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## MASKING

**Introduction.**—Very few analytical reagents, organic or inorganic, are highly selective in their action. Thus, many reagents, which have otherwise useful properties, may have restricted analytical application because they give similar reactions with many ions. For example, many common precipitants, such as ammonium hydroxide, hydrogen sulfide, and 8-hydroxyquinoline quantitatively precipitate many ions, and may be successfully used analytically only under carefully controlled conditions, or for limited separations.

The attainment of selectivity has long been one of the principal objectives of analytical research, but this has proved to be most difficult to achieve. Considerable success has resulted from the development of new reagents which are inherently more selective, but freedom from interference is still best obtained by use of prior separation, the determination and control of optimum reaction conditions, and the use of masking reagents.

Employment of masking reagents affords one of the most promising approaches to the solution of the problem of selectivity, because of the numerous possibilities that the technique presents, and because of the simplicity with which it may be carried out in practice. Masking is ordinarily more rapid than a preliminary separation, and frequently permits a greater accuracy as well.

A *masking agent* is a substance that prevents certain reactions by changing an element or compound into an inactive form without physical separation. Thus, if the chloride ion is added to a solution for the purpose of preventing interference by the silver ion with a determination, the chloride ion is considered a masking agent only if the silver chloride precipitate is not removed by filtration or centrifugation as a preliminary to carrying out the determination.

Many examples of masking can be found in the classical methods of analysis, but most modern masking techniques are based on the formation of complexes by means of complex-forming reagents. Considerable interest has developed in this field during recent years because of the availability of a large number of substances, largely organic, that are capable of forming with metal ions complexes having a wide range of stability.

In the study of a masking procedure, at least two reactions must be considered. These are: (a) the reaction of the substance to be determined with the principal reagent; and (b) the reaction of the substance with the masking reagent (or reagents). The reaction of the principal reagent is called the *principal reaction*. This is of significance in masking techniques when it takes place in the presence of one or more masking reagents, or is, in other words, resistant to masking ac-

tion.<sup>255</sup> Obviously, the successful use of a masking reagent is possible only with the employment of a suitable principal reagent. Thus, the chloride ion (the principal reagent) cannot be used to precipitate silver chloride in the presence of an excess of ammonia, but silver iodide is precipitated under these conditions. The principal reaction of the silver ion with the iodide ion is resistant to the masking action of ammonia.

**Conditions Important in Masking Techniques.**—The successful use of a masking technique in an analytical procedure is dependent upon the proper control of a rather large number of important conditions. These are:<sup>255</sup>

1. **Proper Selection of a Masking Reagent.**—This is illustrated by the fact that a precipitate is obtained when sodium phosphate is added to an aluminum salt solution containing tartaric acid, but no precipitate forms if citric acid is used.

2. **Proper Selection of a Principal Reagent.**—If effective masking is not achieved when a given principal reagent is used in conjunction with a masking agent, the selection of a different reagent may give good results. Thus, the stability of the product of the principal reaction must be considered as well as that of the masking reaction.

3. **Proper Control of pH.**—This is illustrated by the fact that the barium ion is not precipitated as barium sulfate in the presence of EDTA at  $\text{pH} > 7$ , but is precipitated below pH 5.

4. **Combination of More Than One Masking Reagent.**—Thus, the gravimetric determination of bismuth with dimethylglyoxime in basic solution is possible in the presence of EDTA and cyanide, which effectively mask a number of otherwise interfering ions.

5. **Quantity of Masking Agent and Principal Reagent To Be Used.**

6. **Effect of Oxidation State on Stabilities of Complexes Formed.**

7. **Reaction Rate.**—The chromium(III) ion reacts very slowly with EDTA at room temperature and in an acidic medium, and practically no complex is formed under these conditions. When such a solution is heated to boiling, however, a very stable chromium complex is formed.

8. **Solvent Used.**

9. **Temperature.**—Samarium is precipitated as the phosphate from boiling solutions containing EDTA and tartaric acid, but is not precipitated at room temperature when the same complexing agents are used.

**Common Masking Reagents.**—A number of the more common masking reagents used in analytical chemistry are shown in Table 5-6. Not all of these are used for precipitation separations, but those capable of exercising masking action on the more common ions are given.

The masking reagents used to eliminate interference in the precipitation of various metals by different principal reagents are shown in Table 5-7. This table is by no means complete, but it should prove useful in the solution of specific analytical problems, and as a guide to what may be achieved in others. ]

## DEMASKING

**Introduction.**—Demasking is a process in which a masked element or compound is released from its masked form, and regains its activity to enter into reactions with certain other substances. For example, if the zinc ion in a solution is masked

<sup>255</sup> Cheng, K. L., Anal. Chem., 33, 783, 1961.

TABLE 5-6. MASKING AGENTS USED FOR IONS OF VARIOUS ELEMENTS

Abbreviations used: EDTA = ethylenediaminetetraacetic acid; APCA = EDTA and other aminopolycarboxylic acids, as nitrilotriacetic acid and N,N-dihydroxyethylglycine; BAL = 2,3-dimercapto-1-propanol.

Element (or ion)	Masking Reagents
Aluminum	Acetate, BAL, citrate, $C_2O_4^{2-}$ , EDTA, $F^-$ , gluconate, malonate, $OH^-$ , salicylate, sulfosalicylate, tartrate, triethanolamine, and tiron.
Ammonium	HCHO
Antimony	BAL, citrate, EDTA, $I^-$ , $OH^-$ , $S^{2-}$ , $S_2^{2-}$ , $S_2O_3^{2-}$ , and tartrate.
Arsenic	BAL, $OH^-$ , and $S_2^{2-}$ .
Barium	APCA, citrate, and tartrate.
Beryllium	$F^-$ , tartrate, and sulfosalicylate.
Bismuth	APCA, BAL, citrate, $Cl^-$ , dithizone, $I^-$ , $Na_5P_3O_{11}$ , tartrate, triethanolamine, and thiourea.
Boron	$F^-$ and hydroxy acids.
Bromine	Phenol
Cadmium	APCA, BAL, citrate, $CN^-$ , dithizone, $I^-$ , malonate, $SCN^-$ , $S_2O_3^{2-}$ , and tartrate.
Calcium	APCA, citrate, $F^-$ , polyphosphate, and tartrate.
Cerium	APCA, citrate, $F^-$ , tartrate, and tiron.
Chromium	Acetate, APCA, ascorbic acid, citrate, $F^-$ , ( $NaOH + H_2O_2$ ), $Na_5P_3O_{11}$ , sulfosalicylate, tartrate, triethanolamine, and tiron.
Cobalt	APCA, BAL, citrate, $CN^-$ , diethyldithiocarbamate, dimethylglyoxime, ethylenediamine, $F^-$ , $H_2O_2$ , malonate, $Na_5P_3O_{11}$ , $NH_3$ , $NO_2^-$ , $SCN^-$ , $S_2O_3^{2-}$ , and tartrate.
Copper	APCA, BAL, citrate, cobalticyanide, $CN^-$ , $I^-$ , $NaH_2PO_4$ , $NH_3$ , $NO_2^-$ , $S^{2-}$ , $SCN^-$ , $S_2O_4^{2-}$ , sulfosalicylate, tartrate, and thioglycolic acid.
Cyanide	HCHO and $Hg^{++}$ .
Fluoride	$Al^{+++}$ , $Be^{++}$ , $Fe^{+++}$ , $H_3BO_3$ , $Th^{4+}$ , $Ti^{4+}$ , and $Zr^{4+}$ .
Germanium	$C_2O_4^{2-}$ and $F^-$ .
Gold	$Br^-$ , $CN^-$ , and $S_2O_3^{2-}$ .
Hafnium	See zirconium.
Iridium	Citrate, $SCN^-$ , tartrate, and thiourea.
Iron	APCA, ascorbic acid, BAL, $C_2O_4^{2-}$ , citrate, $CN^-$ , $F^-$ , gluconate, malonate, $NH_3$ , $NH_2OH \cdot HCl$ , 8-hydroxyquinoline, 1,10-phenanthroline, $PO_4^{3-}$ , $P_2O_7^{4-}$ , $S^{2-}$ , $SCN^-$ , $S_2O_3^{2-}$ , sulfosalicylate, tartrate, triethanolamine, thioglycolic acid, thiourea, and tiron.
Lead	Acetate, APCA, $As(C_6H_5)_4Cl$ , BAL, citrate, $I^-$ , $Na_5P_3O_{11}$ , $SO_4^{2-}$ , $S_2O_3^{2-}$ , and tartrate.
Magnesium	APCA, $C_2O_4^{2-}$ , $F^-$ , glycols, hexametaphosphate, $OH^-$ , $P_2O_7^{4-}$ , and triethanolamine.
Manganese	APCA, BAL, citrate, $CN^-$ , $C_2O_4^{2-}$ , $F^-$ , $Na_5P_3O_{11}$ , oxidants, $P_2O_7^{4-}$ , sulfosalicylate, tartrate, triethanolamine, and tiron.

TABLE 5-6. (Continued)

Element (or ion)	Masking Reagents
Mercury	Acetone, APCA, BAL, citrate, $\text{Cl}^-$ , $\text{CN}^-$ , $\text{I}^-$ , $\text{SO}_3^{=}$ , tartrate, and triethanolamine.
Molybdenum	APCA, ascorbic acid, citrate, $\text{C}_2\text{O}_4^{=}$ , $\text{F}^-$ , $\text{H}_2\text{O}_2$ , $\text{Na}_5\text{P}_3\text{O}_{11}$ , $\text{NH}_2\text{OH}\cdot\text{HCl}$ , $\text{SCN}^-$ , tartrate, and tiron.
Nickel	APCA, citrate, $\text{CN}^-$ , dimethylglyoxime, $\text{F}^-$ , malonate, $\text{Na}_5\text{P}_3\text{O}_{11}$ , $\text{NH}_3$ , $\text{SCN}^-$ , sulfosalicylate, and tartrate.
Niobium	$\text{C}_2\text{O}_4^{=}$ , $\text{F}^-$ , $\text{H}_2\text{O}_2$ , $\text{OH}^-$ , and tartrate.
Nitrite	Sulfanilic acid.
Osmium	$\text{CN}^-$ , $\text{SCN}^-$ , and thiourea.
Palladium	APCA, citrate, $\text{CN}^-$ , $\text{I}^-$ , $\text{NH}_3$ , $\text{NO}_2^-$ , $\text{SCN}^-$ , $\text{S}_2\text{O}_3^{=}$ , tartrate, and triethanolamine.
Platinum	APCA, citrate, $\text{CN}^-$ , $\text{I}^-$ , $\text{NH}_3$ , $\text{NO}_2^-$ , $\text{SCN}^-$ , $\text{S}_2\text{O}_3^{=}$ , and tartrate.
Rare Earths	EDTA
Rhodium	Citrate, tartrate, and thiourea.
Ruthenium	Thiourea
Scandium	Tartrate
Selenium	$\text{S}^{=}$ and $\text{SO}_3^{=}$ .
Silver	$\text{Br}^-$ , $\text{Cl}^-$ , $\text{CN}^-$ , $\text{I}^-$ , $\text{NH}_3$ , $\text{SCN}^-$ , and thiourea.
Strontium	APCA, citrate, $\text{SO}_4^{=}$ , and tartrate.
Sulfide	S
Sulfite	$\text{HCHO}$ and $\text{Hg}^{++}$ .
Sulfur	$\text{CN}^-$ , $\text{S}^{=}$ , $\text{SO}_3^{=}$ .
Tantalum	Citrate, $\text{F}^-$ , $\text{H}_2\text{O}_2$ , $\text{OH}^-$ , and tartrate.
Tellurium	$\text{I}^-$
Thallium	APCA, citrate, $\text{Cl}^-$ , $\text{CN}^-$ , $\text{NH}_2\text{OH}\cdot\text{HCl}$ , tartrate, and triethanolamine.
Thorium	APCA, citrate, $\text{F}^-$ , $\text{SO}_4^{=}$ , 4-sulfobenzencarsonic acid, tartrate, and triethanolamine.
Tin	BAL, citrate, $\text{C}_2\text{O}_4^{=}$ , $\text{F}^-$ , $\text{I}^-$ , $\text{OH}^-$ , tartrate, triethanolamine, and thioglycolic acid.
Titanium	APCA, ascorbic acid, citrate, chromotropic acid, $\text{F}^-$ , gluconate, $\text{H}_2\text{O}_2$ , $\text{Na}_5\text{P}_3\text{O}_{11}$ , $\text{OH}^-$ , $\text{SO}_4^{=}$ , sulfosalicylate, tartrate, triethanolamine, and tiron.
Tungsten	$\text{F}^-$ , $\text{H}_2\text{O}_2$ , $\text{Na}_5\text{P}_3\text{O}_{11}$ , $\text{NH}_2\text{OH}\cdot\text{HCl}$ , $\text{SCN}^-$ , tartrate, and tiron.
Uranium	Citrate, $\text{CO}_3^{=}$ , $\text{C}_2\text{O}_4^{=}$ , $\text{F}^-$ , $\text{H}_2\text{O}_2$ , and tartrate.
Vanadium	Ascorbic acid, $\text{CN}^-$ , EDTA, $\text{F}^-$ , $\text{H}_2\text{O}_2$ , $\text{NH}_2\text{OH}\cdot\text{HCl}$ , triethanolamine, and tiron.
Zinc	APCA, BAL, citrate, $\text{CN}^-$ , dithizone, $\text{F}^-$ , glycerol, glycol, $\text{Na}_5\text{P}_3\text{O}_{11}$ , $\text{NH}_3$ , $\text{OH}^-$ , $\text{SCN}^-$ , and tartrate.
Zirconium	APCA, citrate, $\text{C}_2\text{O}_4^{=}$ , $\text{F}^-$ , $\text{H}_2\text{O}_2$ , $\text{PO}_4^{3-}$ , $\text{P}_2\text{O}_7^{4-}$ , $\text{SO}_4^{=}$ , tartrate, and triethanolamine.

TABLE 5-7. MASKING AGENTS USED IN PRECIPITATION REACTIONS

Metal Pre- cipitated	Precipitant	Masking Agent	Ions Masked	Reference <sup>256</sup>
Aluminum	Cupferron	EDTA	Phosphate	2
	8-Hydroxyquino- line	EDTA	Metals in steel	22
Antimony	Rhodamine B	H <sub>3</sub> PO <sub>4</sub>	Fe(III)	53
	Na <sub>2</sub> S	Tartrate	Zr	81
Arsenic	Mg <sup>++</sup> + NH <sub>4</sub> <sup>+</sup> OH	EDTA	Alkaline earths	45
	Na <sub>2</sub> S	Tartrate	Zr	81
Barium	SO <sub>4</sub> <sup>==</sup>	EDTA	Al, Bi, Cr, Co, Cu, Fe, Hg, Pb, Ni	63
	SO <sub>4</sub> <sup>==</sup>	EDTA	Sr	1
Beryllium	[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>	EDTA	Al, Ca, Cd, Co, Cu, Fe, Mn, Ni, Ti, Zn	56
	2-Hydroxy-1- naphthalde- hyde	EDTA	Ferrous alloys	26, 27
	8-Hydroxyquino- line	Tartrate	Al	
	NH <sub>4</sub> OH	EDTA	Al, Ca, Fe(III), Mg, Mn	13, 61
	NH <sub>4</sub> OH	EDTA	Al, Co, Cu, Fe, Pb, Mn, Ni, Zn	13, 61
	NH <sub>4</sub> OH	Tartrate	Al	
	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	EDTA	Al, Ca, Fe(III)	30

TABLE 5-7. (Continued)

Metal Pre- cipitated	Precipitant	Masking Agent	Ions Masked	Reference <sup>256</sup>
Bismuth	Diethyldithio- carbamate	CN <sup>-</sup>	Cu	32
	Diethyldithio- carbamate	EDTA	Pb	32
	Dimethylgly- oxime	EDTA + KCN	Al, As, Ba, Cd, Ca, Co, Cu, Pb, Mg, Hg, Ni, Pd, Pt, Ag, Sr, W, Zn	33
	NH <sub>4</sub> OH + Ca <sup>++</sup>	EDTA	Cd, Cu, Pb	58, 59
Calcium	Oxalate	EDTA	Al, As, Be, Bi, Cd, Ce, Cr, Co, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, PO <sub>4</sub> <sup>=</sup> , Sb, Th, U, W, Zn	60
	Oxalate	Sodium gluco- nate	Al, Fe, Ti	86
Cadmium	2-(o-Hydroxy- phenyl)-benz- oxazole	Tartrate	Most metals ex- cept Co, Cu, Ni	85
Cobalt	KNO <sub>2</sub>	F <sup>-</sup>	Nb, Ta, Ti(IV)	31
	KNO <sub>2</sub>	Tartrate	Most metals	31
Copper	Alizarin Blue	Formaldehyde	CN <sup>-</sup>	23
	Electrodeposition	EDTA	Bi	29
	2-(o-Hydroxy- phenyl)-benz- oxazole	EDTA	Ba, Ca, Co, Cr, Fe(III), Mg, Mn, Ni, Pb, Sr, Zn	14

TABLE 5-7. (Continued)

Metal Pre- cipitated	Precipitant	Masking Agent	Ions Masked	Reference <sup>25a</sup>
Magnesium	Arsenate	Citric acid	Al, Fe	80
	8-Hydroxyquino- line	Tartrate	Al, Fe(III)	88
Mercury	Bismuthiol II	EDTA	Most metals ex- cept Ag, Au(I), Tl(I), plati- num group	76
	Mercaptobenzo- thiazol	EDTA	Bi, Cu	12
	Na <sub>2</sub> S	Tartrate	Zr	81
Molybdenum	[Cr(NH <sub>3</sub> ) <sub>5</sub> Cl]Cl <sub>2</sub>	Tartrate	Al, Fe, W	25
	[Cr(NH <sub>3</sub> ) <sub>5</sub> Cl]Cl <sub>2</sub>	EDTA	Al, Ba, Ca, Co, Mg, Mn, Ni, V, Zn	25
	8-Hydroxyquino- line	EDTA	Al, Bi, Co, Cr, Cu, Cd, Fe- (III), Hg(II), Mn, Ni, Pb, Ti, UO <sub>2</sub> <sup>++</sup> , Zn	62
	8-Hydroxyquino- line	EDTA	V	43
Nickel	Dimethylgly- oxime	N,N-Dihydroxy- ethylglycine	Co, Fe(III)	15
	Dimethylgly- oxime	Tartrate	Metals in steel	46
	Dimethylgly- oxime	Tartrate + S <sub>2</sub> O <sub>3</sub> <sup>=</sup>	Cu	18
	α,β-Dioximino- butyranilide	Citrate	Cr, Fe	20



TABLE 5-7. (Continued)

Metal Pre- cipitated	Precipitant	Masking Agent	Ions Masked	Reference <sup>25a</sup>
Nickel	$\alpha,\beta$ -Dioximino- butyranilide	Tartrate	Cr, Fe	20
	Heptoxime	Acetate	Pb	84
	Heptoxime	SCN <sup>-</sup>	Cu	84
	Heptoxime	Tartrate	Al, As, Sb, Bi, Cr, Fe(III), Ti	84
	Nioxime	Tartrate	Al, Fe, Sb	24
Niobium	N-Benzoyl-N- phenylhydrox- ylamine	EDTA	Most metals	41
	Cupferron	EDTA + Tar- trate	Most metals ex- cept Be, PO <sub>4</sub> <sup>=</sup> , Ti, U	39
	H <sub>2</sub> SeO <sub>3</sub>	Tartrate	Zr	4
Palladium	3-Aminopicolinic acid	EDTA	Cu	35
	Bismuthiol II	CN <sup>-</sup>	Ag, Tl	37
	Bismuthiol II	KI	Ag, Hg(II), Pb	38
	Dimethylgly- oxime	EDTA	Most metals	34
	Dimethylgly- oxime	Tartrate	Bi	34
	Nioxime	EDTA	Fe	70
	Quinaldic acid	Nitrilotriacetic acid		34
	Quinolinic acid	EDTA	Cu	36

TABLE 5-7. (Continued)

Metal Pre- cipitated	Precipitant	Masking Agent	Ions Masked	Reference <sup>256</sup>
Phosphate	Mg <sup>++</sup> + NH <sub>4</sub> OH	EDTA	Al, Fe	75
	Mg <sup>++</sup> + NH <sub>4</sub> OH	Tiron	M(III), M(IV)	82
	Molybdate	EDTA	Ca	75
Potassium	Sodium tetra- phenylboron	EDTA	Al, Ba, Ca, Co, Cr, Cu, Fe- (III), Mg, Mn, Ni, Pb, Sb, Ti	19
	Sodium tetra- phenylboron	F <sup>-</sup>	Fe	72
	Sodium tetra- phenylboron	Formaldehyde	NH <sub>4</sub> <sup>+</sup>	10
Silver	1,2,3-Benzotri- azole	EDTA	Bi, Cd, Co, Cu, Fe, Ni, Zn	16, 52
	Bismuthiol II	EDTA	Al, Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Tl, Zn	44
	Bismuthiol II	EDTA	Most metals	57
	Cl <sup>-</sup>	Citrate	Pb	51
	2-Mercaptoben- zimidazole	EDTA	Bi, Cd, Co, Cu, Mn, Ni, Pb, Th, Zn	21
	2-Methylben- zimidazole	EDTA	Bi, Cd, Co, Cu, Mg, Mn, Ni, Pb, Th, Zn	21, 50

TABLE 5-7. (Continued)

Metal Pre- cipitated	Precipitant	Masking Agent	Ions Masked	Reference <sup>25b</sup>
Silver	2-Mercaptoben- zimidazole	Tartrate	Al, Be, U	21
	2-Methylben- zimidazole	Tartrate	Al, Be, U	21
Sodium	Pyroantimonate	EDTA	Ca	47
Strontium	SO <sub>4</sub> <sup>=</sup>	EDTA	Ca	1
Sulfate	Ba <sup>++</sup>	EDTA	Al, Co, Cr, Cu, Fe, Ni	63
	4-chloro-4'- aminodiphenyl	Tartrate	Al	8
	4,4'-Diaminoto- lane	Tartrate	Al	7
	Octa-ammino-μ- amino-μ-nitro- dicobalt-III ni- trate	EDTA	Al, Fe(III)	6
Tantalum	Benzenearsonic acid	EDTA	Most metals ex- cept Ba, Pb, Sr, Ti, Zr	42
Tellurium	Na <sub>2</sub> S	Tartrate	Zr	81
	SO <sub>2</sub> and N <sub>2</sub> H <sub>4</sub> ·HCl	Tartaric acid	Sb	71
Thallium	CrO <sub>4</sub> <sup>=</sup>	Sulfosalicylic acid	Al, Be, Cr(III)	89
	KI	EDTA	Bi, Cu, Fe(III), Pb	69
Thorium	Benzenesulfinic acid	EDTA—Ascorbic acid	Fe(III)	3

TABLE 5-7. (Continued)

Metal Pre- cipitated	Precipitant	Masking Agent	Ions Masked	Reference <sup>28</sup>
Thorium	$\text{NH}_4\text{OH}-\text{H}_2\text{O}_2$	EDTA	Al, Fe	73, 74
	m-Phenylenedi- oxydiacetic acid	Chromotropic acid	Ti	54
Titanium	$\text{NH}_4\text{OH}$	EDTA	Al, Bi, Cd, Cr, Cu, Fe(III), Mn, Ni, Pb	64, 65
	$\text{NH}_4\text{OH}$	EDTA	Fe(III), Mn, Mo, V	55
Tungsten	8-Hydroxyquino- line	EDTA	Al, Bi, Cd, Co, Cr, Cu, Fe- (III), Hg(II), Mn, Ni, Pb, $\text{WO}_4^-$ , $\text{UO}_2^{++}$	66, 67
	8-Hydroxyquino- line	EDTA	Th	48
Uranium	Cupferron	EDTA	Al, Bi, Cd, Cr, Co, Cu, Fe, Mn, $\text{MoO}_4^-$ , Ni, Pb, rare earths, Th, $\text{VO}_3^-$ , $\text{WO}_4^-$ , Zn	40
	Cupferron	Tartaric acid	Al, Sb, Sn(IV), Ta, Zr	11
	8-Hydroxyquino- line	EDTA	Al, Bi, Ca, Cd, Co, Cu, Fe- (III), Hg, Mn, $\text{MoO}_4^-$ , Ni, Pb, $\text{PO}_4^-$ , rare earths, Sr, Th, $\text{VO}_3^-$ , $\text{WO}_4^-$ , Zn, Zr	77, 78, 79

TABLE 5-7. (Continued)

Metal Pre-precipitated	Precipitant	Masking Agent	Ions Masked	Reference <sup>256</sup>
Uranium	H <sub>2</sub> O <sub>2</sub>	EDTA	Sc	9
	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	EDTA	Al, Ba, Cd, Ce, Co, Cr, Cu, Fe, Hg, La, Mg, Mn, Ni, Pb, Sr, Zn	49, 83
	NH <sub>4</sub> OH	EDTA	Most metals except Be and Ti	68
Vanadium	Cupferron	EDTA	Cu	87
Zinc	8-Hydroxyquinoline	Thiourea	Cu	28
Zirconium (Hafnium)	Benzenearsonic acid	H <sub>2</sub> O <sub>2</sub>	Ti	17
	Na <sub>2</sub> HPO <sub>4</sub>	EDTA	Ti	5
	NH <sub>4</sub> OH	H <sub>2</sub> O <sub>2</sub>	Nb, Ta	

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by cyanide, the addition of formaldehyde, because of its reaction with cyanide, frees the zinc ion to react with such reagents as EDTA or Eriochrome Black T.<sup>255</sup>

**Methods Used for Demasking.**—Various methods may be used to effect demasking in analytical procedures. Most important of these are:

1. **Decomposition of the Masking Reagent.**—Thus, EDTA may be destroyed by using a strong oxidizing agent, such as permanganate, in an acid medium, or simply by digesting with a strong acid.

2. **Replacement of the Masked Ion in a Complex by Another Ion With Which the Masking Agent Forms a Stronger Complex.**—The reaction of zirconium with xylenol orange is masked by fluoride, but the addition of beryllium releases the zirconium by forming a more stable fluoride complex.

3. **By Change of pH to Alter the Stability of a Complex.**—For example, vanadium is not precipitated with cupferron in the presence of EDTA at pH above 1.5, but when the pH is reduced to 0.5, precipitation is complete.

4. **By Changing the Oxidation State of the Complexed Ion.**—Copper(II) reacts with 1-(2-pyridylazo)-2-naphthol (PAN) in the presence of thiosulfate at a pH > 7, but in a slightly acidic medium, copper(I) forms a very stable thiosulfate complex that does not give this reaction.

5. **By Volatilization of One of the Components of the Masked System.** For example, fluoride and cyanide can be removed by volatilization in the presence of strong acids, and ammonia can be removed by heating.

**Common Demasking Reagents.**—A number of demasking reagents in analytical reactions is shown in Table 5-8.

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TABLE 5-8. DEMASKING REAGENTS

Complexing Agent	Ion Demasked	Demasking Reagent	Application
Ammonia	Ag <sup>+</sup>	Br <sup>-</sup>	Detection of Br.
	Ag <sup>+</sup>	H <sup>+</sup>	Detection of Ag.
	Ag <sup>+</sup>	I <sup>-</sup>	Detection of I and Br.
	Ag <sup>+</sup>	SiO <sub>2</sub> (amorph.)	Differentiation of cryst. and amorph. SiO <sub>2</sub> (+ CrO <sub>4</sub> ).
Carbonate	Cu <sup>++</sup>	H <sup>+</sup>	Free Cu <sup>++</sup> .
Chloride (conc.)	Ag <sup>+</sup>	H <sub>2</sub> O	Precipitation of AgCl.
Cyanide	Ag <sup>+</sup>	H <sup>+</sup>	Precipitation of Ag.
	Cd <sup>++</sup>	H <sup>+</sup>	Free Cd <sup>++</sup> .
	Cd <sup>++</sup>	HCHO (OH <sup>-</sup> )	Detection of Cd (+ diphenylcarbazide) in presence of Cu.
	Cu <sup>+</sup>	H <sup>+</sup>	Precipitation of Cu.
	Cu <sup>++</sup>	HgO	Determination of Cu.
	DMG <sup>207</sup>	Pd <sup>++</sup>	Detection of CN <sup>-</sup> (+ Ni <sup>++</sup> ).
	Fe <sup>++</sup>	Hg <sup>++</sup>	Free Fe <sup>++</sup> .
	Fe <sup>3+</sup>	HgO	Determination of Fe.
	Hg <sup>++</sup>	Pd <sup>++</sup>	Detection of Pd (+ diphenylcarbazide).
	Ni <sup>++</sup>	HCHO	Detection of Ni (+ dimethylglyoxime).
	Ni <sup>++</sup>	HgO	Determination of Ni.
	Ni <sup>++</sup>	H <sup>+</sup>	Free Ni <sup>++</sup> .
	Ni <sup>++</sup>	Ag <sup>+</sup> , Hg <sup>++</sup> , Pb <sup>++</sup>	Detection of Ag, Hg, Pb (+ dimethylglyoxime).
	Ni <sup>++</sup>	Ag halides	Detection of Ag halides (+ dimethylglyoxime).
	Ni <sup>++</sup>	Ag <sup>+</sup>	Detection and determination of Ni (+ dimethylglyoxime) in presence of Co.
	Pd <sup>++</sup>	HgO	Determination of Pd.
	Pd <sup>++</sup>	H <sup>+</sup>	Precipitation of Pd.
	Zn <sup>++</sup>	CCl <sub>3</sub> CHO·H <sub>2</sub> O	EDTA titration of Zn.
	Zn <sup>++</sup>	H <sup>+</sup>	Free Zn <sup>++</sup> .
EDTA	Al <sup>3+</sup>	F <sup>-</sup>	Titration of Al.
	Ba <sup>++</sup>	H <sup>+</sup>	Precipitation of BaSO <sub>4</sub> (+ SO <sub>4</sub> <sup>-</sup> ).
	Co <sup>++</sup>	Ca <sup>++</sup>	React. Co <sup>++</sup> with diethyldithiocarbamate.
	Mg <sup>++</sup>	F <sup>-</sup>	Titration of Mg, Mn, and Zn.
	Th <sup>4+</sup>	SO <sub>4</sub> <sup>-</sup>	Titration of Th.



TABLE 5-8. (Continued)

Complexing Agent	Ion Demasked	Demasking Reagent	Application
EDTA	Ti <sup>4+</sup>	Mg <sup>++</sup>	Precipitation of Ti (+ NH <sub>4</sub> -OH).
	Zn	CN <sup>-</sup>	Titration of Mg, Mn, and Zn.
	Many ions	MnO <sub>4</sub> <sup>-</sup> + H <sup>+</sup>	Free ions.
Ethylenediamine	Ag <sup>+</sup>	SiO <sub>2</sub> (amorph.)	Differentiation of cryst. and amorph. SiO <sub>2</sub> (+ CrO <sub>4</sub> <sup>-</sup> ).
Fluoride	Al <sup>3+</sup>	OH <sup>-</sup>	Precipitation of Al(OH) <sub>3</sub> .
	Al <sup>3+</sup>	Be <sup>++</sup>	Precipitation of Al (+ oxine).
	Fe <sup>3+</sup>	OH <sup>-</sup>	Precipitation of Fe(OH) <sub>3</sub> .
	Mo, V, and W	H <sub>3</sub> BO <sub>3</sub>	Free MoO <sub>4</sub> <sup>=</sup> , VO <sub>3</sub> <sup>-</sup> , WO <sub>4</sub> <sup>=</sup> ions.
	Sn <sup>4+</sup>	H <sub>3</sub> BO <sub>3</sub>	Precipitation of Sn (+ H <sub>2</sub> S).
	U	Al <sup>3+</sup>	Determination of U (dibenzoylmethane).
	Zr <sup>4+</sup>	Ca <sup>++</sup>	Detection of Ca <sup>++</sup> (+ Alizarin S).
	Zr <sup>4+</sup> Zr, Hf	OH <sup>-</sup> Be <sup>++</sup> , Al <sup>3+</sup>	Precipitation of Zr(OH) <sub>4</sub> . Detection of Zr and Hf (+ xyleneol orange).
H <sub>2</sub> O <sub>2</sub>	Ti, Zr, and Hf	Fe <sup>3+</sup>	
Nitrite	Co <sup>3+</sup>	H <sup>+</sup>	Free of Co <sup>3+</sup> .
Oxalate	Al <sup>+++</sup>	OH <sup>-</sup>	Precipitation of Al(OH) <sub>3</sub> .
Phosphate	Fe <sup>3+</sup>	OH <sup>-</sup>	Precipitation of FePO <sub>4</sub> .
	U	Al <sup>3+</sup>	Determination of U (dibenzoylmethane).
Sulfate (conc. H <sub>2</sub> SO <sub>4</sub> )	Ba <sup>++</sup>	H <sub>2</sub> O	Precipitation of BaSO <sub>4</sub> .
Tartrate	Al <sup>3+</sup>	H <sub>2</sub> O <sub>2</sub> + Cu <sup>++</sup>	Precipitation of Al(OH) <sub>3</sub> .
Thiocyanate	Fe <sub>3</sub> <sup>+</sup>	OH <sup>-</sup>	Precipitation of Fe(OH) <sub>3</sub> .
Thiosulfate	Cu	OH <sup>-</sup>	Detection of Cu (+ PAN).
	Ag <sup>+</sup>	H <sup>+</sup>	Free Ag <sup>+</sup> .

<sup>257</sup> Dimethylglyoxime.

## Chapter 6

# SEPARATION BY ELECTROLYSIS

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One of the methods commonly employed for quantitative separations is that of electrolysis. These electrolytic methods can be applied to the quantitative removal and determination of one or more different metallic ions from solution or may be used, with carefully controlled conditions, to effect a separation of ions of one metal from those of several other metals.

Before discussing electrolytic methods, it is essential to recall certain fundamental laws and facts related to electrolysis. The *coulomb* is the quantity of electricity that will cause the deposition or removal of 0.001118 g. of silver at an electrode. An *ampere*, the unit of current, is 1 coulomb per second. The *ohm* is the unit of resistance; a column of mercury 106.3 cm. long at 0°C. weighing 14.4521 g. and of uniform cross-section has a resistance of 1 ohm. The *volt* or unit of electromotive force (emf) causes a current of 1 ampere to flow through a resistance of 1 ohm. The *volt-coulomb* or *joule* is the unit of electrical energy, and the *volt-ampere* or *watt* is the unit of electrical power.

*Ohm's Law* gives the relation between current, resistance and electromotive force.

$$\text{Current} = \frac{\text{electromotive force}}{\text{resistance}} \text{ or } I = \frac{E}{R},$$

where  $I$  is in amperes,  $E$  in volts, and  $R$  in ohms.

The *faraday*, 96,493 coulombs, is the amount of electricity equivalent to Avogadro's number of electrons transferred in either an oxidation or a reduction process. Because this quantity of electrons must be removed to oxidize a gram equivalent of any substance and the same number of electrons must be taken to reduce a gram equivalent, a *faraday* is that quantity of electricity used in transforming a gram equivalent of any substance at an electrode.

The two laws of electrolysis, usually referred to as Faraday's Laws, can be stated as follows:

1. The quantity of a given substance that is liberated at an electrode is proportional to the quantity of electricity that is passed through the system.

2. The amounts of different substances that are deposited by the same quantity of electricity are proportional to the chemical equivalent weights of these substances. These statements would appear to be self-evident, but they are true only if the current efficiency does not vary and is 100% for the substance being meas-

ured. For example, if a faraday of electricity is passed through each of three solutions containing copper(II), silver(I), and zinc(II), respectively, the amounts of metals deposited on the cathodes will be 63.54/2 g. of copper, 107.88 g. of silver, and 65.38/2 g. of zinc if 100% current efficiency is achieved in each case. Likewise, if only 0.100 faraday of electricity were passed through each of these solutions, only 0.100 as much of each of these metals would be deposited.

## CURRENT EFFICIENCY

Two or more electrochemical processes may occur simultaneously at an electrode. If the efficiency of one of these processes is to be determined, it is necessary to know the ratio of the number of coulombs required for this particular process as compared with the total number of coulombs that were passed through the solution.

Many electrolytic separations can be performed without any concern for or knowledge of the operating current efficiency. For example, in the separation of copper from an aqueous nitric acid solution of copper ions, the reduction of both copper and nitrate ions may occur at the cathode. Since the total amount of current required for the deposition of copper is not usually measured, the current efficiency for this process is relatively unimportant.

On the other hand, if an electrolytic separation or determination is made which depends on measuring the current passed through the solution for a given length of time, it is necessary to know accurately the efficiency of this process. Usually in such procedures, only one electrochemical reaction occurs at the electrode, and experimental conditions are so maintained that virtually one hundred per cent current efficiency is achieved.

Rate of stirring of the electrolyte, concentration of electrochemically active material, temperature, composition of the electrode, and current density are some of the factors that are important in controlling current efficiency. Current density is defined as the current in amperes per square centimeter of electrode surface. As the current density increases, the number of electrons passing through a unit area of the electrode surface increases, and the probability that only one electrochemical process can give or take this quantity of electrons decreases. For this reason, a second process may occur at the electrode, and the current efficiency for the first process decreases.

## THEORY OF ELECTROLYSIS

### ELECTRODE POTENTIALS

If any chemical element that is a conductor of electricity is placed in contact with a solution containing its own ions, a potential difference develops at the interface between the electrode and solution. The magnitude and sign or direction of this potential depend upon the relative tendency of the atoms of the element to give off or accept electrons to form ions of the element. Depending on the nature of the element and the concentration of its ions in solution, the potential of the electrode may be positive, zero, or negative relative to the solution.

If a piece of copper metal is immersed in a dilute solution of cupric sulfate, the copper metal will become positively charged; if a piece of zinc is immersed in a dilute solution of zinc sulfate, the zinc metal will become negatively charged.

There are two major factors that determine the electrode potential relative to

another electrode. First is the activity of the electrolytic solution pressure of the element, which is the tendency of the element to furnish ions. At a given temperature and pressure this is a characteristic constant for a stable form of an element but varies if the electrode is strained mechanically or if a metastable crystalline form of the metal is present. Second is the activity of the dissolved ions of the element, which in turn varies with the concentration at constant temperature. A table of standard potentials at 25°C. that apply to the condition of unit activity (approximately 1 molar) of the ions and one atmosphere pressure for gases is given in Table 6-1. These standard potentials are the potentials that the element or electrode develop with regard to the solution and are designated as  $E_{\text{Cu}}^0$ ,  $E_{\text{Zn}}^0$ ,  $E_{\text{H}_2}^0$ , etc. Because it is impossible to measure the potential of a single electrode in contact with a solution, these standard values are relative, and the standard hydrogen ion-hydrogen electrode is arbitrarily taken as the standard of reference. Because standard potentials vary with temperature, the temperature at which the potential is measured should be specified.

The potentials shown in Table 6-1 are standard reduction potentials and all reactions are written as reductions. For oxidations, which is the same as considering the reactions in Table 6-1 written in the opposite direction, the magnitude

TABLE 6-1. STANDARD REDUCTION POTENTIALS AT 25°C.

<i>Electrode Reaction</i>	<i>E<sup>0</sup>, volt</i>
$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.045
$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.925
$\text{Ca}^{++} + 2\text{e}^- \rightarrow \text{Ca}$	-2.87
$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.714
$\text{Zn}^{++} + 2\text{e}^- \rightarrow \text{Zn}$	-0.763
$\text{Fe}^{++} + 2\text{e}^- \rightarrow \text{Fe}$	-0.440
$\text{Cd}^{++} + 2\text{e}^- \rightarrow \text{Cd}$	-0.403
$\text{Co}^{++} + 2\text{e}^- \rightarrow \text{Co}$	-0.277
$\text{Ni}^{++} + 2\text{e}^- \rightarrow \text{Ni}$	-0.250
$\text{Sn}^{++} + 2\text{e}^- \rightarrow \text{Sn}$	-0.136
$\text{Pb}^{++} + 2\text{e}^- \rightarrow \text{Pb}$	-0.126
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.000
$\text{BiO}^+ + 2\text{H}^+ + 3\text{e}^- \rightarrow \text{Bi} + \text{H}_2\text{O}$	+0.32
$\text{Cu}^{++} + 2\text{e}^- \rightarrow \text{Cu}$	+0.337
$\text{I}_3^- + 2\text{e}^- \rightarrow 3\text{I}^-$	+0.536
$\text{Hg}_2^{++} + 2\text{e}^- \rightarrow 2\text{Hg}$	+0.789
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.7991
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.065
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.229
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.360
$\text{PbO}_2 + \text{HSO}_4^- + 3\text{H}^+ + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	+1.685

of the potential will remain the same but the sign will be opposite. Thus, the standard potential for the reaction  $\text{Zn}^{++} + 2\text{e}^- \rightarrow \text{Zn}$  is -0.763 volt but the standard potential for the oxidation of Zn ( $\text{Zn} \rightarrow \text{Zn}^{++} + 2\text{e}^-$ ) is +0.763 volt.

### VOLTAIC AND ELECTROLYTIC CELLS

A *voltaic cell* consists of two electrodes and one or more solutions and is capable of spontaneously converting chemical energy more or less completely into elec-

trical energy and supplying this energy to an external source. In these cells, a chemical reaction involving an oxidation at one electrode and a reduction at the other electrode occurs. The electrons evolved in the oxidation step are transferred at the electrode surface, pass through the external circuit and back to the electrode where reduction takes place. When one of the chemical components that is responsible for these reactions is depleted, the cell is no longer capable of supplying electrical energy to an external source and the cell is "dead."

If electrical energy is supplied from an external source, the cell through which it flows is called an *electrolytic cell*. A given cell may function at one time as a voltaic cell and at another as an electrolytic cell. The lead storage battery is the most familiar example of this phenomenon. When the cell is used to furnish current to an external source, acting as a voltaic cell, the following reaction proceeds from left to right:



The lead electrode gives off electrons and the lead dioxide electrode accepts the electrons. This reaction can be reversed during the charging process, when electrical energy is supplied from an external source, and under these conditions, the cell is functioning as an electrolytic cell. It should be realized that the electrical energy needed to charge a lead storage battery must be greater than that supplied by the battery when it is acting as a voltaic cell and, furthermore, this electrical energy must be applied in the direction opposite to that given off by the voltaic cell.

In any electrolysis, a voltaic cell is built up from the products of the electrolytic cell which accumulate at the electrodes. If the external current is turned off, the products tend to produce current in the opposite direction. Thus, the voltage necessary to cause electrolysis must exceed the voltage produced by the voltaic cell and must also overcome the IR drop (the resistance of the solution to the passage of current) as well as any irreversible phenomena (e.g., overvoltage) that may occur at the electrode surfaces.

In order to determine what voltage must be supplied to a cell to cause electrolysis, it is necessary to know first what reactions will occur at the two electrodes. If these reactions are known, it is possible to calculate the potential of each electrode and thereby determine the emf of the voltaic cell which exerts its potential in opposition to the applied voltage. For example, in the electrolysis of 0.100 *M*  $\text{CuSO}_4$  in 1 *N*  $\text{H}_2\text{SO}_4$  with platinum electrodes, the reaction at the cathode will be  $\text{Cu}^{++} + 2\text{e}^- \rightarrow \text{Cu}$ , and at the anode,  $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ . *The back emf, or the emf of the voltaic cell which opposes the applied voltage of the electrolysis, will be developed when the two reactions occurring at the electrodes in the electrolysis are proceeding in opposite directions.*

The potential, *E*, of any electrode is given by the generalized form of the Nernst equation

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{\text{ox}}}{a_{\text{Red}}},$$

where  $E^0$  is the standard electrode potential (see Table 6-1), *R* is the molar gas constant (8.316 volt-coulombs per degree), *T* is the absolute temperature, *n* is the number of electrons transferred in the electrode reaction, *F* is the Faraday (96,493 coulombs), and  $a_{\text{ox}}$  and  $a_{\text{Red}}$  are the activities of the oxidized and reduced forms, respectively, of the electrode reaction. If concentrations are substituted for activities, common logarithms for natural logarithms, and numerical values substituted

for the constants, assuming the temperature to be 25°C., the Nernst equation becomes

$$E = E^0 + \frac{.059}{n} \log \frac{[\text{ox}]}{[\text{Red}]}$$

Using this equation to calculate the potential of the Cu electrode, where the reaction is  $\text{Cu}^{++} + 2e^- \rightarrow \text{Cu}$ , we see that

$$E = 0.337 + \frac{.059}{2} \log \frac{[\text{Cu}^{++}]}{[\text{Cu}]};$$

[Cu] represents the concentration of the reduced form of this electrode reaction and  $[\text{Cu}^{++}]$  the concentration of the oxidized form. Because [Cu] is the concentration of copper in the metal, or the mole fraction of copper, the denominator of the log term is unity. Thus, the potential of a copper electrode can be calculated very simply if we know the concentration of the copper ions in which the copper electrode is immersed:  $E = 0.337 + 0.0295 \log [\text{Cu}^{++}]$ . It is obvious that the potential of a Cu electrode equals 0.337 volt or the  $E_{\text{Cu}^0}$  value when the concentration of the copper ions is unity. In the example chosen above,  $[\text{Cu}^{++}] = 0.1$  and the potential of the copper electrode is  $E = 0.337 + .0295 \log 0.1 = 0.308$  volt. However, in the voltaic cell which is established in this electrolysis cell, the reaction at the copper electrode is an oxidation. The sign of this calculated potential, therefore, must be reversed and becomes  $-0.308$  volt.

For the other electrode where oxygen is evolved,

$$E = 1.229 + \frac{.059}{4} \log \frac{[\text{O}_2][\text{H}^+]^4}{[\text{H}_2\text{O}]^2}$$

This expression can be simplified by realizing that  $[\text{O}_2]$  is the same as the pressure of  $\text{O}_2$  gas, which is virtually 1 atmosphere,\* and that the concentration of  $\text{H}_2\text{O}$  is essentially constant. Then,  $E = 1.229 + .059 \log [\text{H}^+]$  or  $E = 1.229 - .059 \text{ pH}$ . In 1 N  $\text{H}_2\text{SO}_4$ , the  $[\text{H}^+] = 1$  and the  $\text{pH} = 0$  and the potential of this electrode is 1.229 volt. At this electrode, the voltaic cell would require oxygen to be reduced and the sign of the calculated potential does not change.

The emf of any cell is merely the algebraic sum of the potentials of the two electrodes composing the cell, provided the signs of these two potentials are adjusted to take into account that one reaction is an oxidation and the other is a reduction. Thus, the emf of the voltaic cell, or the back emf established when 0.100 M copper sulfate is electrolyzed, is the sum of +1.229 volt and  $-0.308$  volt or +0.921 volt.

As the electrolysis of the copper sulfate proceeds, the concentration of the copper ions in solution decreases and the concentration of the hydrogen ions increases. This means that the potential of both electrodes is continuously changing during the electrolysis; the potential of the copper electrode becomes more negative and that of the oxygen electrode more positive. The net result of this effect is that the magnitude of the back emf increases constantly as the electrolysis proceeds and, consequently, an increasingly larger voltage must be applied to keep the electrolysis operating.

\* Actually, oxygen is being evolved at the electrode against a partial pressure of oxygen in the atmosphere; therefore, for accurate calculations of the potential of the oxygen electrode,  $[\text{O}_2]$  cannot be taken as unity.

**Overvoltage and IR Drop.**—The voltage applied to a cell in order to cause any electrolysis must be sufficient to overcome the sum of any overvoltage effects, IR drop, and back emf, all of which operate to prevent electrolysis from occurring.

Overvoltage is the potential over and above the potential calculated by the Nernst equation from standard electrode potentials needed to maintain a certain deposition at an electrode. For example, in the previous illustration with copper sulfate, the potential calculated for the oxygen electrode was 1.23 volt. The potential actually required to deposit oxygen at the platinum anode in this case may be 2.00 volt. Thus, the overvoltage would be  $2.00 - 1.23$  or 0.77 volt.

Both anodic and cathodic processes exhibit overvoltage. If an anodic process

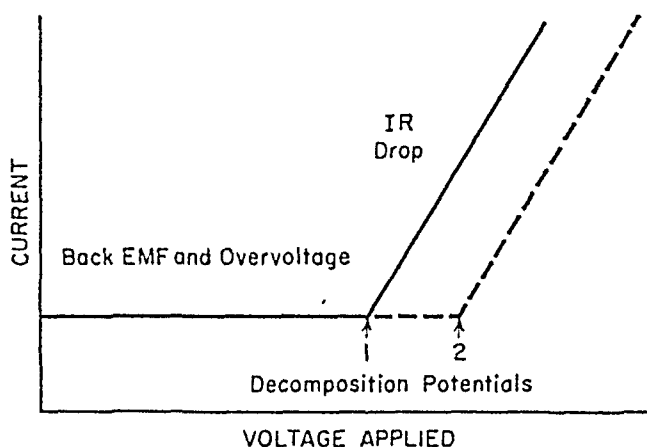


FIG. 6-1. Current as a Function of Voltage Applied in an Electrolysis Cell.

Virtually no current flows until a voltage is applied in excess of the decomposition potential. If the IR drop and the decomposition potential for the process designated by "1" is equal or greater than the decomposition potential for "2," the second electrolytic process will occur simultaneously with the first.

shows an overvoltage effect, the applied potential necessary to cause electrolysis will always be a more positive value than the calculated potential. For cathodic processes, overvoltage causes the applied potential to be more negative than the calculated value.

Deposition of metals from metallic ion solutions generally show small overvoltage effects of 0.1 volt or less, whereas the evolution of gases at an electrode is usually associated with an overvoltage about ten times as large. In addition to this variable, overvoltage depends on the chemical composition of the electrode, the condition (rough or smooth, bright or platinized) of the electrode, temperature, and current density. (M. Knobel, P. Caplan, and M. Eiseman, in *Trans. Am. Electrochem. Soc.*, 43, 55, 1923, give values of the overvoltage for the deposition of several gases on a variety of electrodes and over a wide range of current densities.)

Although overvoltage phenomena complicate the calculation of the voltage necessary for electrolysis to occur, its effect makes feasible certain separations that would not be expected from standard electrode potentials. For example, Table 6-1 indicates that the deposition of hydrogen should require much less negative potential than is required for the deposition of cadmium or zinc and, therefore, that the discharge of hydrogen should prevent the deposition of cadmium or zinc. Actually, both of these metals can be separated from aqueous solution because the

overvoltage of hydrogen causes the potential at which hydrogen is really deposited to be more negative than that of cadmium and, if the pH of the solution is adjusted, of zinc. By using a mercury cathode, on which the overvoltage of hydrogen is particularly high, it is possible to remove electrolytically even alkali and alkaline earth metals from aqueous solution.

The IR drop is merely the product of the current passing through the cell and the resistance of the cell. Obviously, the IR drop will be very small when small currents are flowing but becomes very significant for large currents. In Fig. 6-1, the relation of IR drop to applied voltage in electrolysis is shown. In most electrolytic separations from aqueous solution, the resistance of the cell is small (less than 5 ohms) and the IR drop is usually considered to be small. However, if only 0.2 ampere is flowing, the IR drop is 1 volt with a 5 ohm resistance, and the applied voltage may have exceeded the decomposition potential of another cell that could occur in the same solution. This effect often leads to very poor current efficiencies and to contaminated deposits.

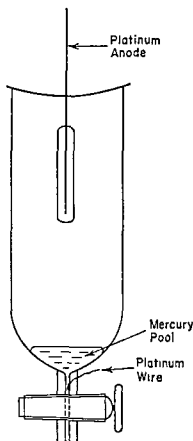


FIG. 6-2. Cell for Electrolysis with a Mercury Cathode.

## EQUIPMENT FOR ELECTROLYTIC SEPARATIONS

In order to make simple electrolytic separations, it is necessary to have a source of direct current, an adjustable resistance, a cell for electrolysis, including the electrodes and usually some means for stirring the solution. If the current or applied voltage is to be controlled, an appropriate ammeter and voltmeter are needed. The direct current is most conveniently supplied from storage batteries because they give a steady voltage. However, a small motor generator or a rectifier unit may be operated from alternating current to supply the direct current. If the separation

is to be done with a controlled electrode potential, a *potentiostat* is usually used to maintain this desired potential and to supply the necessary current. Many of the potentiostats that have been described in the literature and are commercially available are explained in Lingane's monograph on *Electroanalytical Chemistry*.<sup>1</sup>

The electrolysis cell is frequently a beaker—preferably a tall-form. For some electrolytic separations where a mercury electrode is used, a special cell similar to that shown in Fig. 6-2 is used. In some cases, a platinum container or dish may serve as the electrolysis cell and simultaneously as one electrode. For solutions containing hydrofluoric acid, polyethylene beakers should be used. Generally, the electrolysis cell is covered with a split watch glass to exclude dirt and to minimize loss of solution through spray during the actual electrolysis.

The electrodes are usually either platinum or mercury. Many separations can

<sup>1</sup> Lingane, J. J., *Electroanalytical Chemistry*, 2nd Ed., Interscience Publishers, Inc., New York, 1958.



be performed using a platinum gauze cathode and a platinum foil anode. When mercury is used as the cathode, a platinum foil or spiral is used as the anode. There are some separations which require silver electrodes. If the potential of either electrode is to be controlled during the electrolytic separation, it is essential to have a reference electrode of known potential. This electrode, which is frequently a saturated calomel electrode ( $E = 0.246$  volt), should be equipped with a capillary tube to permit close contact with the solution and the operating electrode and to minimize diffusion of solution either into or out of the reference electrode. If stirring of the solution is necessary, this can be accomplished by a simple motor stirrer and a glass propeller, by a magnetic stirrer, or with a rotating electrode. This last method is very commonly used where commercially available equipment for electrodeposition is employed.

### FACTORS AFFECTING SEPARATIONS

Electrolytic separations are usually made for one of two reasons: Either the analyst wishes to remove an element or a group of elements which will interfere in a subsequent determination, or the separation is being made prior to the determination of the element separated. In the latter case, it is important to make the separation under conditions which insure that the deposit is pure, adherent to the electrode, and quantitative. This requires careful consideration of the factors that influence the nature of the deposit; the most important of these are the current density, the chemical nature of the ion in solution (*i.e.*, complexed as  $\text{Ag}(\text{CN})_2^-$  or  $\text{Ni}(\text{NH}_3)_4^{++}$  or as a simple hydrated ion), the rate of stirring, the temperature, and the presence of depolarizers which minimize the evolution of gases. Where the separation is made solely for removing interferences, the control of these experimental conditions may be less important, but is still highly significant in minimizing the time required to complete the separation.<sup>2</sup> The time required for electrodeposition onto solid electrodes can be greatly decreased if the electrode is vibrated vigorously.<sup>3</sup>

The optimum conditions for achieving the best deposit of a metal vary from one metal to another. For example, a pure, bright, and adherent deposit of copper can be obtained when electrolyzing a nitric acid solution of cupric ions. If a suitable deposit of Ag is to be obtained, the electrolysis must be carried out from a solution in which the silver ions are complexed as  $\text{Ag}(\text{CN})_2^-$ . Similarly, the best deposits of iron are obtained from an oxalate complex and those of nickel from an ammonia complex.

After the electrolysis is complete, the deposited metal(s) must be removed from the solution without contaminating the solution if further analyses are to be made on the solution, and without loss of the deposited metal if this deposit is to be analyzed. If the deposit has been made on a platinum electrode and is to be weighed, the electrode must be washed thoroughly as it is removed from the solution. Furthermore, because of the voltaic cell which is present and which would cause dissolution of the deposited metal if the applied voltage were interrupted, the electrode should be washed without breaking the electric circuit. This is best done by lowering slowly the electrolysis cell from the electrodes while washing the

<sup>2</sup> Casto, C. C., *Analytical Chemistry of the Manhattan Project*, Vol. I, Chap. 23, McGraw-Hill, 1950. This chapter gives a good account of the factors that influence the electrolytic separation of impurities from uranium.

<sup>3</sup> Facsko, F., *Proc. 15th Intern. Cong. Pure and Appl. Chem. (Anal. Chem.)*, Vol. I, 639-653, Lisbon, 1956.

electrodes with a stream of water from a wash bottle. The electrodes are then usually rinsed with alcohol or acetone, which retards the air oxidation of the wet deposit, prior to drying them at an elevated temperature. The common practice for the determination consists in weighing the electrode before and after deposition to obtain the weight of the deposit. If there is any possibility that some of the platinum has been lost during the electrolysis, the deposit can be weighed, dissolved, and then the electrode alone weighed.

If the deposit has been made into a mercury electrode, the electrolysis solution is removed from the mercury by siphoning, or the mercury is drained from the electrolysis cell. The mercury is then washed with alcohol and diethyl ether and air-dried prior to weighing. Alternatively, the mercury, after being removed from the electrolysis cell, can be distilled, and the metallic residue can then be analyzed by other methods.<sup>4</sup>

If the electrolysis is performed to remove interferences prior to subsequent determinations, the same general precautions as mentioned before must be observed in removing the electrodes from the solution. It is necessary in these cases to prevent any loss or contamination of the electrolysis solution.

### SEPARATIONS WITHOUT REGULATION OF ELECTRODE POTENTIALS

When a direct current is passed through a solution containing two platinum electrodes, first the electrochemical process with the most positive reduction potential will occur at the cathode, then the next most positive process will occur there, etc. If, for example, a solution containing cupric, hydrogen, zinc, and bisulfate ions is electrolyzed, first copper will be deposited at the cathode. As this metal deposits, the concentration of cupric ions in solution decreases and, according to the Nernst equation, the potential at which the copper deposits becomes more negative. When the potential of the cathode is reduced to the value required for the reduction of hydrogen ions, hydrogen gas will form at the cathode. If oxygen is being evolved at the anode during this electrolysis, the hydrogen-ion concentration remains virtually constant in solution during the *electrodeposition of hydrogen ions because the amount of hydrogen ions made at the anode is equal to that consumed at the cathode*. Thus, the potential of the cathode does not change appreciably so long as hydrogen is evolved, which is usually until all the water is electrolyzed. Therefore, the potential of the cathode cannot become sufficiently negative to allow the deposition of the zinc ions. It should be evident, then, that metallic ions with a positive reduction potential may be separated, without external control of the cathode potential, from metallic ions having negative reduction potentials. Reference to standard reduction potentials as shown in Table 6-1 is not sufficient to decide what separations are possible by this technique. It must be remembered that the hydrogen overvoltage causes the reduction of hydrogen ions to occur at potentials more negative than those calculated by the Nernst equation from standard potentials. In order to separate two metals by this technique, the hydrogen overvoltage on the cathode plus the reversible reduction potential of the hydrogen ions must be less than the negative reduction potential of any of the metallic ions that are to remain

<sup>4</sup> Furman, N. H., Bricker, C. E., and McDuffie, B., J. Wash. Acad. Sci., 38, 159, 1948. Schmidt, W. E., and Bricker, C. E., J. Electrochem. Soc., 102, 623, 1955.

in solution. For example, copper ions in a solution 1 *M* in hydrogen ions may be separated only from those metallic ions whose reduction potentials are more negative than about  $-0.8$  volt even though the reversible reduction potential of hydrogen is  $0.0$  volt in this medium. This is, of course, due to the fact that the overvoltage of hydrogen on copper at a certain current density is about  $0.8$  volt.

In addition to separating metals whose reduction potentials are on different sides of the hydrogen electrode, it is possible to separate several metals on the anode. Under suitable conditions,  $\text{PbO}_2$ ,  $\text{MnO}_2$  and  $\text{Ti}_2\text{O}_3$  can be deposited at the anode and thereby separated from nearly all other metallic ions.

Some separations without controlled cathode potential are possible only if the metallic ions are complexed or if the pH of the solution is controlled. Copper and lead are readily deposited from nitric-sulfuric acid solutions: the copper at the cathode, and the lead as  $\text{PbO}_2$  at the anode. Under these conditions, nickel, manganese, and zinc are not deposited. If tin is complexed as the fluoride, copper and lead may be electrodeposited without potential control and without depositing tin. Copper may be separated from large amounts of iron if ethylenediamine-tetraacetic acid sufficient to complex the iron is added. Complexing the metallic ions may even reverse the order of the deposition of the metals. For example, copper ( $E^0 = +0.34$  v.) is deposited in acid solution prior to cadmium ( $E = -0.40$  v.), but in cyanide media, the tetracyanocadmiate ions are reduced at more positive potentials than the tricyanocuprite ions.

### MERCURY CATHODE

Many metallic ions that cannot be electrolyzed on a platinum or other solid metal electrode can be deposited into a mercury cathode. This is due to the high overvoltage of hydrogen on a mercury surface and also to the fact that metallic ions are deposited on mercury at more positive potentials. To illustrate this latter effect, consider the potential required for the deposition of zinc ions on a zinc cathode and on a mercury cathode.

On a zinc electrode,

$$E_{\text{Zn electrode}} = E_{\text{Zn}}^0 + \frac{.059}{2} \log \frac{[\text{Zn}^{++}]}{[\text{Zn}]}$$

As stated before  $[\text{Zn}] = 1$  and  $E_{\text{Zn electrode}} = E_{\text{Zn}}^0 + .0295 \log [\text{Zn}^{++}]$ .

For a mercury cathode,

$$E_{\text{Hg cathode}} = E_{\text{Zn}}^0 + \frac{.059}{2} \log \frac{[\text{Zn}^{++}]}{[\text{Zn}(\text{Hg})]}$$

If the concentration of the zinc in the amalgam [*i.e.*,  $\text{Zn}(\text{Hg})$ ] be maintained at less than  $10^{-3}$  *M*, this equation would become, at this concentration,

$$E_{\text{Hg cathode}} = E_{\text{Zn}}^0 + \frac{.059}{2} \log \frac{[\text{Zn}^{++}]}{10^{-3}}$$

or

$$E_{\text{Hg cathode}} = E_{\text{Zn}}^0 + 3(0.0295) + .0295 \log [\text{Zn}^{++}].$$

In other words, by keeping the concentration of zinc in the amalgam low, the zinc ions will plate out at a potential equal to  $3(0.0295)$  volt more positive with a mercury cathode than with a massive zinc cathode.

These effects on a mercury cathode permit even the deposition of alkali and alkaline earth metals from neutral or alkaline solution. However, the most im-

portant separations using a mercury cathode are made from acidic solutions (about 0.3 *N* sulfuric acid) where it is possible to deposit quantitatively Cr, Fe, Co, Ni, Cu, Zn, Ga, Ge, Mo, Rh, Pd, Ag, Cd, In, Sn, Re, Ir, Pt, Au, Hg, Tl, Bi, and Po into the mercury. In addition, Os, Pb, Se, Te, and As are completely removed from solution during the electrolysis even though they may not be entirely in the mercury. Osmium may be volatilized as the tetroxide at the anode; some lead may plate as  $\text{PbO}_2$  on the anode; selenium and tellurium are reduced to the metal but stay suspended in the solution, arsenic may be reduced to arsine and escape. A few elements, Mn, Ru, and Sb, are incompletely removed from solution by this type of electrolysis.

A mercury cathode electrolysis is often used to remove numerous interfering elements from solution prior to the estimation of elements such as aluminum, uranium, vanadium, the alkaline earths, and the alkalis. A cell similar to that shown in Fig. 6-2 can be used for this procedure.

### SEPARATIONS WITH CONTROLLED ELECTRODE POTENTIALS

In the previous section, it was stated that metals whose potentials were on different sides of the hydrogen ion-hydrogen electrode could be separated electrolytically. No reference was made to separating, for example, silver and copper or lead and cadmium. Separations of two or more different metallic ions can be made even though their reduction potentials are on the same side of hydrogen if provision is made to control the cathode potential so that only the ions reduced at the most electropositive potential are deposited. For these conditions, an assembly similar to that shown in Fig. 6-3 is necessary.

The potential of the electrode is determined by measuring the emf of the cell established by the electrode and a reference electrode. If the emf of the cell and the potential of the reference electrode are known, the potential of the operating electrode can be calculated. It is necessary, then, to control the potential of the electrode so that it never becomes sufficiently negative to allow the deposition of the next element. This control of the electrode is achieved by adjusting the voltage applied to the electrolysis cell, which can be done either manually with a battery and a variable resistor or electronically with a potentiostat.

Consider, for example, a solution which is 1 *M* in each of the ions silver, copper, cadmium, zinc, and hydrogen. A diagram of the course of the electrolysis of this solution using platinum electrodes is shown in Fig. 6-4. If oxygen is evolved at the anode, the potential at which this oxidation will occur will be the  $E_{\text{oxygen}}^0$  plus the overvoltage or about 1.8 volt. This potential of the anode, which is shown as a horizontal line in Fig. 6-4, will remain essentially constant because the factors that affect this deposition (hydrogen-ion concentration, pressure of oxygen, and concentration of water) do not change appreciably. Silver will deposit first on the cathode at a potential of about 0.8 volt. Thus, the emf needed for electrolysis will be about 1.00 volt plus any IR drop. As silver is deposited, the concentration of the silver ion decreases and the potential of the cathode becomes more negative. When the silver ion concentration is reduced to  $10^{-7}$  *M*, the potential of the cathode is 0.387 volt and the emf needed for electrolysis is 1.41 volt. Copper will not start to deposit until the potential of the cathode is 0.337 volt or until the emf applied is 1.46 volt. Thus, if the potential of the cathode can be controlled so that it never becomes more negative than +0.40

volt, no copper will be deposited, and since the silver ion is reduced to nearly  $10^{-7} M$ , the separation of silver is virtually complete.

After the silver is separated, the copper could then be separated from the cadmium and zinc on a fresh electrode by controlling the potential of the cathode at another value which is slightly more positive than that required for the deposition of cadmium. It is obvious that the copper ion concentration would be reduced to an extremely low value before cadmium would start to deposit (theoretically, to  $10^{-25} M$ ).

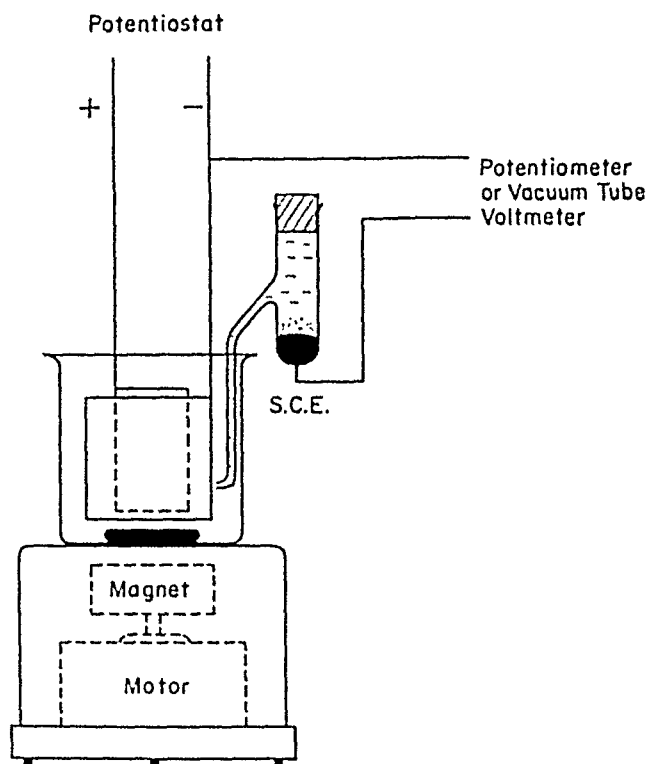


FIG. 6-3. Apparatus for Electrolysis at Controlled Potential.

This apparatus can be modified easily so that a mercury cathode can be used instead of a platinum gauze cathode.

No cathode control would be necessary to separate the cadmium from the zinc because as the cadmium ion concentration became very low, hydrogen would start to deposit before zinc. As explained previously, the overvoltage of hydrogen would cause the evolution of hydrogen to occur at  $-0.7$  to  $-0.8$  volt rather than at its reversible potential of  $0.0$  volt. With the potential of the anode and cathode remaining constant, the emf required, when hydrogen and oxygen are the products of the electrolysis, would remain steady at about  $2.5$  volt.

By far the most convenient way to control the potential of the cathode during an electrolysis is with a potentiostat. The emf that the cell, consisting of a reference electrode and the cathode, should have at the end of a given electrolytic separation is set on the potentiostat and this instrument controls the voltage applied to the electrolysis cell so that this emf is held constant.

Separations with controlled electrode potentials are very satisfactorily done with a mercury cathode. By including a silver or some other coulometer in series with

the electrolysis circuit, it is comparatively simple to perform a series of separations and analyses without replacing the mercury cathode between successive separations. Because the same current flows through the electrolysis cell and the coulometer, a given separation at a controlled potential is carried out, and the amount of metal deposited in the mercury is calculated by using Faraday's Laws and the amount of reaction that is observed in the coulometer. The next elec-

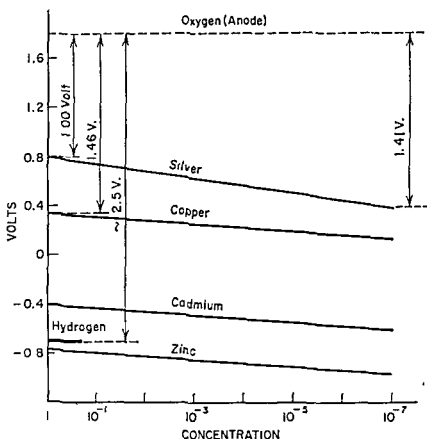


FIG. 6-4 Schematic Representation of an Electrolytic Separation.

The voltage that must be applied to the electrolysis cell for the deposition of silver is indicated. If this applied voltage is never greater than that required for the deposition of copper, only silver will be deposited. Similarly, the voltage required for the separation of copper from cadmium can be deduced. The removal of cadmium from zinc does not require potential control.

tolysis is then performed at a new controlled potential without changing the electrolysis cell but, again, the coulometer is used to determine the amount of electrolysis that occurs.

The potential of an anode can be controlled in a similar manner. This technique is particularly useful in stripping one metal from a group of metals that may be present in an amalgam. In this case, the most electronegative metal is oxidized from the amalgam first, followed by the less electronegative metals. It is important to realize that certain metals, especially iron, cobalt, and nickel, cannot be oxidized from mercury prior to the oxidation of mercury itself. This phenomenon greatly limits the utility of controlling the potential during the stripping of a mercury amalgam.

Electrolyses with controlled electrode potentials have wide and varied applications. The most common inorganic applications are in the analysis of many

alloys and in the determination of the nature and thickness of oxide films on various metals. The use of controlled electrode potentials is now quite prevalent in preparative organic chemistry. If a certain organic compound can undergo a series of reductions (or oxidations), each at a definite potential, it is then possible to reduce the starting material selectively and efficiently to some desired compound by controlling the potential of the cathode during the reduction. Because this procedure for reducing (or oxidizing) organic compounds produces essentially only the desired product, it is much more economical than most reductions performed chemically, where side reactions producing undesired products usually occur.<sup>5</sup>

### INTERNAL ELECTROLYSIS

Another method to control a cathode potential is that employed in internal electrolysis. If an active metal is connected to a platinum electrode and both are immersed in the same solution, the potential of the platinum electrode cannot be more negative than that established by the dissolution of the active metal. Thus, if the separation of copper from cadmium is to be realized, an anode of lead could be connected to a platinum electrode. The dissolution of the lead would establish a potential on the platinum sufficiently negative to deposit the copper but not adequate to reduce the cadmium ions. It is possible, therefore, to control the potential of the cathode by merely choosing the proper anode.

In actual practice, the anode which is frequently placed in a neutral electrolyte is separated from the solution to be analyzed by a porous cup. This prevents major contamination of the solution in the anode compartment by the solution to be electrolyzed and vice versa. In order to prevent concentration polarization and to minimize the time for a separation, the solution being electrolyzed should be stirred.

This simple method of controlling a cathode potential is used principally to plate out small quantities of noble metals in a solution of a more active metal. This technique is particularly suitable in those solutions where a platinum anode would be attacked in conventional electroanalysis, as in solutions containing a large concentration of chloride ions. Specific examples where this technique is advantageous are the determination of copper and bismuth in lead, of tin in aluminum, of cadmium in zinc, and of lead in antimony.

Internal electrolysis is not confined to cathodic depositions. Recently,  $Tl_2O_3$  as well as  $MnO_2$ ,  $PbO_2$ , and  $Ni_2O_3$  have been deposited on an anode by using very strong oxidizing agents as a catholyte.<sup>6</sup>

### OTHER SEPARATION TECHNIQUES

There are several other techniques used in separating materials which do not necessarily involve electrolysis but which are based on the migration of charged particles in an electric field.

*Electrophoresis* is the migration of large molecules and small aggregates of molecules under the influence of an electric field applied to a medium in which the particles are suspended. Proteins, viruses, clay suspensions, rubber emulsions, and

<sup>5</sup> A complete bibliography of publications through 1961 on controlled-potential electrolysis and coulometry at controlled potential has been compiled by Y. Israel and L. Meites and published by Analytical Instruments, Inc., Wolcott, Conn.

<sup>6</sup> Lipchinskii, A., Zhur. Anal. Khim., 12, 83, 1957; 13, 402, 1958.

colloids are some examples of substances that may be separated into pure components by means of this technique. Because of the great interest in this means of separation and because of the various requirements of the wide variety of applications, no single apparatus or procedure can be described for electrophoretic separations. In general, the material to be separated is suspended in a water solution where the pH and the electrolyte concentration are controlled carefully. This water suspension is placed in a comparatively long, small-bore tube, and an electric field is applied. The various charges or, more correctly, the various ratios of charge to size on the suspended particles will cause different degrees of migration. After a certain time, particles having a similar ratio of charge to size will have migrated to a small section of the tube, while particles with other ratios will be at another location. These sections of the tube must then be separated and the components isolated. All vibration of the apparatus, temperature gradients, and any other experimental variables that would cause random migration of the particles must be controlled carefully. For details of this technique, one of the recent monographs on electrophoresis should be consulted.

In order to minimize the factors that cause random migration in electrophoresis and thereby permit separations that would otherwise be impossible, the suspension of the material to be separated is placed on paper or some other supporting medium and the bands or zones of pure material are developed in this support. Separations which are performed by differential electrical migration in stabilized media are frequently referred to as *electrochromatography* as well as electrophoresis. This technique is used extensively for two widely different applications, the separation of inorganic ions and the separation of complex organic mixtures. In the latter case, employed extensively in biochemical investigations, it is possible to separate, purify, and isolate labile, water-soluble substances not easily prepared by other methods.

A modification or extension of electrochromatography is *continuous electrochromatography* or *curtain electrochromatography*. In this method, the solution is introduced continuously at the top and usually in the center of some vertically mounted supporting medium. This medium may be a sheet of paper, a layer of starch, a bed of very small glass beads, or the like, supported between two plates of glass or other material. The solution flows downward by gravity through the supporting medium while the electrical potential is applied at right angles to this flow. The principle of chromatography (selective adsorption and elution) as well as that of electrophoresis contributes to the resolution of the solution. As the solution drains off the bottom of the supporting medium, it is collected in a series of containers arranged along the horizontal width. If the separation is complete, individual components of the solution will be found in one of the containers or at least in two or three adjacent containers. This technique is useful in separating the components from a comparatively large volume of solution.<sup>7</sup>

The principle of electrical migration of charged particles has also been applied in *electrodialysis*, *electro-ultrafiltration*, and *electrodecantation*. These techniques find wide application in the preparation and purification of organic substances such as proteins, hormones, enzymes, starches, resins, and cellulose.<sup>8</sup>

<sup>7</sup> Details of this method can be found in monographs on electrochromatography and, more specifically, in recent articles by H. H. Strain and A. Karler.

<sup>8</sup> Details of these techniques can be found in the chapter by R. E. Stauffer in *Technique of Organic Chemistry*, Vol. III, Part I, Separation and Purification, Interscience Publishers, Inc., New York, 1956.



## Chapter 7

# SOLVENT EXTRACTION

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The use of solvent extraction as a general method of separation in analytical chemistry has increased markedly in recent years as analysts have come to recognize it as a powerful separation technique. Extraction systems have become much more sophisticated since the early application of ethers for the solvent extraction of ferric chloride from hydrochloric acid solutions. Many new reagents are now commercially available and have assumed general use in analytical chemistry. Literature in this field is increasing.<sup>1</sup>

Table 7-11 includes a large number of reagents that have been used in separations by solvent extraction. These reagents are listed under two classifications: chelates; and ion-association systems. In chelate extractions, the metal cation usually forms a complex with the reagent that is readily soluble in an organic solvent. In ion-association systems, the metal exists as an uncharged species in combination with some anion due to electrostatic attraction.

The form of solvent extraction most widely used in analytical chemistry is liquid-liquid extraction. The aqueous solution is brought into contact with an immiscible organic solvent, which either contains the extractant in solution or else serves as the extractant, in order to transfer one or more of the solutes into the organic solvent. Separations achieved are customarily rapid, and essentially free of phenomena such as coprecipitation and adsorption. Solvent extraction can be applied equally well to trace level and large amounts of material. The apparatus required is simple and economical; in practice a separatory funnel is the only equipment needed.

### SOLVENT EXTRACTION TABLES

In Tables 7-1 through 7-10, the extraction characteristics are shown for several of the more common reagents and a few relatively new ones. The elements enclosed in blocks can be extracted to better than 95% by the particular reagent

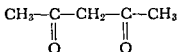
<sup>1</sup> The following general references might be consulted profitably: Biennial reviews on Solvent Extraction, *Anal. Chem.*, 1958, 1960, 1962; Morrison, G. H., and Freiser, H., *Solvent Extraction in Analytical Chemistry*, John Wiley and Sons, Inc., New York, 1957; Sandell, E. B., *Colorimetric Determination of Traces of Metals*, 3rd Ed., Interscience Publishers, Inc., New York, 1959; Symposium on Solvent Extraction in the Analysis of Metals, ASTM Special Technical Publication No. 238, 1958; Treybol, R. E., *Engineering Aspects (Source of New Reagents)*, *Ind. Eng. Chem.*, 51, Part II, 378, 1959.

under the designated conditions in a single equilibration. A brief discussion of each of the reagents referred to in the Tables is given.

Many other reagents have been used in separations by solvent extraction. A number of the more important of these are shown in Table 7-11. Undoubtedly some of these reagents will become extractants in general use in future years. The reader should be aware that, with respect to analytical application, a large number of new extraction systems remain to be investigated. Data for many potential separations exist in source material not normally read by analytical chemists.

The physical constants for a number of organic solvents are given in Table 7-12.

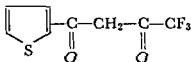
### ACETYLACETONE



Acetylacetone is a colorless liquid that boils at 135 to 137°C. (745 mm. Hg.), and has a density of 0.976 at 25°C. It is only slightly soluble in water but soluble in many organic solvents. Extractions are usually made with the pure liquid as both extractant and solvent, or in solution with carbon tetrachloride, chloroform, benzene, or xylene. It is stable and can be stored indefinitely.

Acetylacetone forms chelates with some 60 metals. In the preceding periodic chart (Table 7-1), however, only those metals extracted to greater than 90% in a single extraction are inclined. These chelates are very soluble in organic solvents so that acetylacetone is useful in extracting macro amounts of metals as well as in micro scale extractions.

### THENOYLTRIFLUOROACETONE (TTA)



Thenoyltrifluoroacetone is a crystalline solid, melting at 42.5 to 43.2°C. It is generally used in a 0.1 to 0.5 M solution in benzene or toluene. The reagent is a useful extractant over a wide range of acidity and has received much attention in the extraction of the heavy elements, i.e., the actinides.

### 8-QUINOLINOL (OXINE)



8-Quinolinol (oxine) is a white crystalline compound melting at 74 to 76°C. It is generally used in solution with chloroform. The solution in chloroform is sensitive to light, and should be stored in brown bottles, preferably in a refrigerator.























TABLE 7-11. METAL EXTRACTION SYSTEMS

*Chelate Systems*

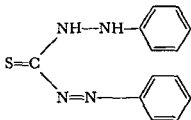
Acetylacetone  
Thenoyltrifluoroacetone  
Quinalizarin  
Morin  
8-Quinolinol  
Dimethylglyoxime  
Cyclohexanedionedioxime  
Furildioxime  
Benzoyldioxime  
Salicylaldoxime  
1-Nitroso-2-naphthol  
N-Nitrosophenylhydroxylamine, ammonium salt (cupferron)  
N-Nitrosonaphthylhydroxylamine, ammonium salt (neocupferron)  
N-Benzoylphenylhydroxylamine  
Benzohydroxamic acid  
1-(2-Pyridylazo)-2-naphthol  
Diphenylthiocarbazone (Dithizone)  
Toluene-3,4-dithiol  
Sodium diethyldithiocarbamate  
Potassium xanthate  
Phenylthiourea

*Ion-Association Systems*

Ethyl ether  
Isopropyl ether  
Ethyl acetate  
4-Methyl-2-pentanone (Hexone)  
Diisopropylketone  
Tributylphosphate  
Carbon tetrachloride  
Benzene  
*n*-Butanol  
2-Ethylhexanol  
2-Octanol  
Diisobutylcarbinol  
Dibutylcarbitol  
Pentaether  
Perfluorocarboxylic acids  
Alkylphosphoric acids  
Tri-*n*-octylphosphine oxide  
High molecular weight amines  
Tetraphenylarsonium (phosponium) chlorides

Oxine forms chelates with many metals and is widely used in analytical separations by solvent extraction, although it is not very selective. Its selectivity has been greatly extended by application of masking agents, such as ethylenediamine-tetraacetic acid (EDTA). The reagent is often used as a 1% solution; in many cases, however, more concentrated solutions, as high as 10%, can be profitably used, particularly in the case of alkaline earth separations.

### DIPHENYLTHIOCARBAZONE (DITHIZONE)

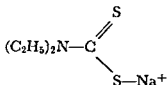


Diphenylthiocarbazone is a purplish black crystalline compound that decomposes at temperatures above 165°C. It is soluble in organic solvents and insoluble in aqueous solutions except for aqueous ammonia. The reagent is used almost exclusively in chloroform or carbon tetrachloride solution.

As a precautionary measure, due to its sensitivity to oxidation, dithizone should be purified before use by filtering the chloroform solution and then extracting it with aqueous ammonia. Dithizone in the aqueous solution is precipitated by acidifying with HCl. The dried reagent should be kept in a dark, tightly stoppered bottle. As an alternative to drying the precipitate, dithizone may be extracted from its aqueous acidic solution with chloroform, and used as the chloroform solution.

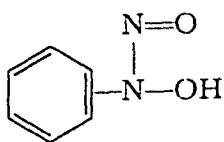
Formation of metal chelates is possible in both acid and basic solutions since dithizone is tautomeric. Most analytical applications are made from acidic solutions because the chelates formed are more stable and more soluble in organic solvents.

### SODIUM DIETHYLDITHIOCARBAMATE



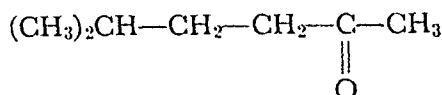
Sodium diethyldithiocarbamate is a white crystalline compound, generally used in the form of a 2% aqueous solution. The reagent is used in basic solutions in most applications, although extractions can be carried out in acidic solutions if done rapidly to avoid decomposition of the reagent.

Since the reagent is not selective, it is often used in conjunction with masking agents.

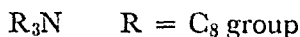
**N-NITROSOPHENYLHYDROXYLAMINE (CUPFERRON)**

Cupferron is a white crystalline solid melting at 163 to 164°C. The ammonium salt is the customary form of the analytical reagent. It is soluble in water and alcohol and generally used in an aqueous solution (6%). The metal cupferrates are soluble in ether and chloroform.

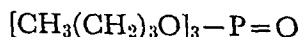
Solutions of the reagent should be kept refrigerated. Extractions are best carried out in the cold to avoid decomposition of the metal chelate. Chloroform is the preferred solvent for extraction of the precipitated chelates.

**4-METHYL-2-PENTANONE (HEXONE)**

4-Methyl-2-pentanone is a clear liquid boiling at 116°C. It is somewhat soluble in water, about 2% by weight. The reagent is commonly used in the form of the organic solvent itself. Extractions are possible from a wide variety of acidic systems. The reagent has found much use in flame photometry since hexone solutions of many cations can be aspirated directly into the flame.

**TERTIARY HIGH MOLECULAR WEIGHT AMINES**

Tertiary high molecular weight amines, such as the octylamine, tri-*n*-octylamine, triisooctylamine and methyl-di-*n*-octyl amines, are often referred to as "liquid anion exchangers." The extraction characteristics closely resemble the adsorption capabilities of the solid anion exchange resins. The amines are usually dissolved in either polar or non-polar solvents; benzene and xylene are the most widely used solvents. Extraction coefficients are acid-dependent and vary greatly. Extractions can be carried out from essentially any acidic medium as long as anionic complexes of the metal are present. The amines extract mineral and organic acids. A 0.1 *M* amine solution is commonly used in separations. The addition of capryl alcohol (about 2% by volume) to the solvent is suggested to avoid possible emulsion formation.

**TRI-*n*-BUTYL PHOSPHATE**

Tri-*n*-butyl phosphate is a clear liquid which boils at 154 to 157°C. (10 mm. Hg). It is one of the most widely used reagents of the alkylphosphoric acid ester family. The reagent is soluble in most organic solvents and is often used in extractions

TABLE 7-12. PHYSICAL CONSTANTS OF ORGANIC SOLVENTS \*

## HYDROCARBONS

	Formula	Density	Boiling Point, °C.	$n_D$	Dielectric Constant	Solubility in Water
Cyclohexane	$C_6H_{12}$	0.7831 <sub>15</sub>	80.738	1.42623 <sub>20</sub>	2.0	0.01 g./100 g. at 20°
Hexane	$C_6H_{14}(CH_2)_4CH_3$	0.6603 <sub>20</sub>	69.0	1.37480 <sub>20</sub>	1.9	0.138 g./l. at 15°
Heptane	$C_7H_{16}(CH_2)_5CH_3$	0.684 <sub>20</sub>	98.52	1.3867 <sub>20</sub>	1.9	0.052 g./l. at 15°
Benzene	$C_6H_6$	0.8944 <sub>0</sub>	80.103	1.50110 <sub>20</sub>	2.3	0.180 g./100 g. at 25°
Toluene	$C_6H_5CH_3$	0.866 <sub>20</sub>	110.8	1.49782 <sub>16</sub>	2.4	0.47 g./l. at 16°
Xylene, ortho	$C_6H_4(CH_3)_2$	0.8745 <sub>20</sub>	144	1.50543 <sub>20</sub>	2.6	
meta	$C_6H_4(CH_3)_2$	0.8684 <sub>18</sub>	138.8	1.49721 <sub>20</sub>	2.4	0.196 g./l. at 25°
para	$C_6H_4(CH_3)_2$	0.8611 <sub>20</sub>	138.5	1.49581 <sub>20</sub>	2.3	0.19 g./l. at 25°
1,3,5-Trimethylbenzene (mesitylene)	$(CH_3)_3C_6H_3$	0.8634 <sub>20</sub>	164.6	1.4967 <sub>20</sub>	2.3	Insoluble

## SUBSTITUTED HYDROCARBONS

Carbon disulfide	$CS_2$	1.2626 <sub>20</sub>	46.3	1.62950 <sub>18</sub>	2.6	2.2 g./l. at 22°
Carbon tetrachloride	$CCl_4$	1.595 <sub>20</sub>	76-77	1.46305 <sub>18</sub>	2.2	0.8 g./l. at 20°
Chloroform	$CHCl_3$	1.49845 <sub>18</sub>	61.26	1.41643 <sub>18</sub>	4.8	10 g./l. at 15°
Dichloromethane (methylene chloride)	$CH_2Cl_2$	1.336 <sub>20</sub>	40.1	1.42456 <sub>20</sub>	9.1	20 g./l. at 20°
Nitromethane	$CH_3NO_2$	1.14476 <sub>18</sub>	101.25	1.38189 <sub>20</sub>	35.9	9.5 ml./100 ml.
1,2-Dichloroethane (ethylene chloride, ethylene dichloride)	$ClCH_2CH_2Cl$	1.257 <sub>20</sub>	83.5-83.7	1.44759 <sub>18</sub>	10.4	9 g./l. at 0°
Nitroethane	$CH_3CH_2NO_2$	1.5028 <sub>20</sub>	114	1.3920 <sub>20</sub>	28.1	4.5 ml./100 ml. at 20°
Tetrachloroethylene	$C_2Cl_4$	1.6311 <sub>18</sub>	121.20	1.50566 <sub>20</sub>	2.3	0.015 g./100 g.
1,1,2,2-Tetrachloroethane (acetylene tetrachloride)	$C_2H_2Cl_4$	1.600 <sub>20</sub>	146.3	1.49678 <sub>18</sub>	8.2	0.288 g./100 g. at 25°
1,1,1-Trichloroethane (methyl chloroform)	$CH_3CCl_3$	1.3249 <sub>20</sub>	74.3	1.43765 <sub>21</sub>	7.5	0.132 g./100 g. at 20°
1,1,2-Trichloroethane	$ClCH_2CHCl_2$	1.443 <sub>20</sub>	113.5	1.4714 <sub>20</sub>		0.436 g./100 g. at 20°
Trichloroethylene	$C_2HCl_3$	1.4556 <sub>20</sub>	87	1.4767 <sub>21</sub>	3.4	1 g./l.
<i>o</i> -Dichlorobenzene	$C_6H_4Cl_2$	1.3003 <sub>20</sub>	180.48	1.54911 <sub>21</sub>	9.9	Almost insoluble
<i>m</i> -Dichlorobenzene	$C_6H_4Cl_2$	1.28280 <sub>20</sub>	173.00	1.54337 <sub>25</sub>	5.0	0.0123 g./100 ml. at 25°
<i>p</i> -Dichlorobenzene	$C_6H_4Cl_2$	1.4581 <sub>20</sub>	174.12	1.52849 <sub>20</sub>	2.4	0.077 g./1000 g. at 30°
1,2,3-Trichlorobenzene	$C_6H_3Cl_3$		219			Insoluble
1,2,4-Trichlorobenzene	$C_6H_3Cl_3$		213			Insoluble
1,3,5-Trichlorobenzene	$C_6H_3Cl_3$	1.574 <sub>10</sub>	208.5	1.5671		Insoluble



*Monohydric Alcohols*

Methanol	CH <sub>3</sub> OH	64.7	1.33118 <sub>14,6</sub> <sup>o</sup>	32.6	Completely soluble
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	78.325	1.36242 <sub>18,4</sub> <sup>o</sup>	24.3	Completely soluble
1-Propanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> OH	97.2	1.38556 <sub>20</sub> <sup>o</sup>	20.1	Completely soluble
2-Propanol (isopropyl alcohol)	(CH <sub>3</sub> ) <sub>2</sub> CHOH	82.3	1.3747 <sub>25</sub> <sup>o</sup>	18.3	Completely soluble
1-Butanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH	117.71	1.39922 <sub>20</sub> <sup>o</sup>	17.1	79 g./l. at 20°
2-Methyl-1-propanol (isobutyl alcohol)	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> OH	107-108	1.39768 <sub>15</sub> <sup>o</sup>	17.7	95 g./l.
1-Pentanol ( <i>n</i> -amyl alcohol)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> OH	138.06	1.40999 <sub>20</sub> <sup>o</sup>	13.9	2.19% by weight at 25°
3-Methyl-1-butanol (isoamyl alcohol)	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> OH	130.5	1.40853 <sub>15</sub> <sup>o</sup>	14.7	2.67% by weight
1-Hexanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>2</sub> OH	155-158	1.41816 <sub>20</sub> <sup>o</sup>	13.3	0.706% by weight
4-Methyl-2-pentanol (methyl isobutyl carbinol)	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CHOHCH <sub>3</sub>	131.4	1.4089 <sub>25</sub> <sup>o</sup>		18 g./l.
2,4-Dimethyl-3-pentanol (diisopropyl carbinol)	[(CH <sub>3</sub> ) <sub>2</sub> CH] <sub>2</sub> CHOH	140	1.42259		Slightly soluble
2,6-Dimethyl-4-heptanol (diisobutyl carbinol)	[(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> ] <sub>2</sub> CHOH	172-174	1.423 <sub>31</sub> <sup>o</sup>		Insoluble
2-Ethyl-1-hexanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(C <sub>2</sub> H <sub>5</sub> )CH <sub>2</sub> OH	184.6	1.4300		0.14% at 25°
1-Octanol (capryl alcohol)	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>2</sub> OH	194-195	1.42913 <sub>20</sub> <sup>o</sup>	10.3	0.0538% by weight
Cyclohexanol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CHOHCH <sub>3</sub>	178.5	1.4260 <sub>20</sub> <sup>o</sup>	8.2	Insoluble
Benzyl alcohol	C <sub>6</sub> H <sub>5</sub> OH	161.5	1.46562 <sub>2,6</sub> <sup>o</sup>	15.0	0.567% at 15°
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	205.2	1.54033 <sub>20</sub> <sup>o</sup>	13.1	4% at 17°

*Polyhydric Alcohols*

1,2-Ethanedil (ethylene glycol)	HOCH <sub>2</sub> CH <sub>2</sub> OH	197.2	1.11710 <sub>15</sub> <sup>o</sup>	37.7	Completely soluble
1,2-Propanedil (propylene glycol)	CH <sub>3</sub> CHOHCH <sub>2</sub> OH	189	1.0364 <sub>20</sub> <sup>o</sup>	32.0	Completely soluble
1,2,3-Propanetriol (glycerol)	CH <sub>2</sub> OHCHOHCH <sub>2</sub> OH	290	1.26134 <sub>20</sub> <sup>o</sup>	42.5	Completely soluble

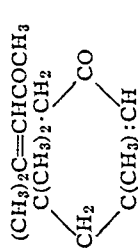
*Alcohol Ethers*

Furfuryl alcohol	C <sub>4</sub> H <sub>3</sub> OCH <sub>2</sub> OH	170	1.4873 <sub>20</sub> <sup>o</sup>		Completely soluble
Tetrahydrofurfuryl alcohol	C <sub>4</sub> H <sub>7</sub> OCH <sub>2</sub> OH	177-178	1.4505 <sub>25</sub> <sup>o</sup>		Very soluble
2-Methoxyethanol (ethylene glycol monomethyl ether, methyl cellosolve)	CH <sub>3</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	124.3	1.4017 <sub>20</sub> <sup>o</sup>	16.0	Completely soluble
2-Ethoxyethanol (cellosolve, ethylene glycol monomethyl ether)	C <sub>2</sub> H <sub>5</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	135.1	1.40751 <sub>20</sub> <sup>o</sup>		Completely soluble
2-Butoxyethanol (butyl cellosolve, ethylene glycol mono- <i>n</i> -butyl ether)	C <sub>4</sub> H <sub>9</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	170.6	1.4190 <sub>25</sub> <sup>o</sup>		Mixes with an equal volume of water
Diethylene glycol (2,2'-dihydroxyethyl ether)	HO(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> OH	244.5	1.4475 <sub>20</sub> <sup>o</sup>		Soluble
2-(2-Methoxyethoxy) ethanol (methyl carbitol, diethylene glycol monomethyl ether)	CH <sub>3</sub> O(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> OH	193.2	1.4264 <sub>27</sub> <sup>o</sup>		Completely soluble
2-(2-Ethoxyethoxy) ethanol (carbitol, diethylene glycol monoethyl ether)	C <sub>2</sub> H <sub>5</sub> O(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> OH	201.9	1.4254 <sub>26</sub> <sup>o</sup>		Very soluble
2-(2-Butoxyethoxy) ethanol (butyl carbitol, diethylene glycol mono- <i>n</i> -butyl ether)	C <sub>4</sub> H <sub>9</sub> O(CH <sub>2</sub> ) <sub>2</sub> O(CH <sub>2</sub> ) <sub>2</sub> OH	231.2	1.4290 <sub>27</sub> <sup>o</sup>		Completely soluble

TABLE 7-12. PHYSICAL CONSTANTS OF ORGANIC SOLVENTS (CONT.)

## HYDROXY COMPOUNDS

	Formula	Density	Boiling Point, °C.	n	Dielectric Constant	Solubility in Water
Triethylene glycol (2,2'-ethylenedioxydiethanol)	$\text{HO}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OH}$	1.1274 <sub>15</sub> <sup>*</sup>	280-290	1.4578 <sub>13</sub> <sup>*</sup>		Completely soluble
<i>Keto Alcohol</i>						
4-Hydroxy-4-methyl-2-pentanone	$\text{CH}_3\text{COCCH}_2\text{C}(\text{CH}_3)_2\text{OH}$	0.9185 <sub>20</sub> <sup>*</sup>	169.1	1.4241 <sub>620</sub> <sup>*</sup>	18.2	Completely soluble
<i>Ethers</i>						
Ethyl ether	$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	0.71925 <sub>15</sub> <sup>*</sup>	34.5	1.35124 <sub>17</sub> <sup>1*</sup>	4.3	7.42% by weight at 20°
n-Propyl ether	$\text{CH}_3(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{CH}_3$	0.73178 <sub>15</sub> <sup>*</sup>	91	1.3803 <sub>29</sub> <sup>*</sup>	3.4	0.25% by weight
Isopropyl ether	$(\text{CH}_3)_2\text{CHOCH}(\text{CH}_2)_2$	0.72813 <sub>20</sub> <sup>*</sup>	67.5	1.36888 <sub>20</sub> <sup>*</sup>	3.9	0.65% by volume at 25°
n-Butyl ether	$\text{CH}_3(\text{CH}_2)_3\text{O}(\text{CH}_2)_3\text{CH}_3$	0.7692 <sub>20</sub> <sup>*</sup>	142	1.39975 <sub>20</sub> <sup>*</sup>	3.1	Practically insoluble
$\beta,\beta'$ -Dichlorodiethyl ether	$\text{Cl}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{Cl}$	1.2192 <sub>20</sub> <sup>*</sup>	178.5	1.45750 <sub>20</sub> <sup>*</sup>	21.2	1.02%
p-Dioxane	$\text{C}_4\text{H}_8\text{O}_2$	1.03375 <sub>20</sub> <sup>*</sup>	101.32	1.42241 <sub>20</sub> <sup>*</sup>	2.2	Soluble
Diethyl cellosolve	$\text{C}_2\text{H}_5\text{O}(\text{CH}_2)_2\text{OC}_2\text{H}_5$	0.8417 <sub>20</sub> <sup>*</sup>	121.4			
Dibutyl carbitol	$\text{C}_4\text{H}_9\text{O}(\text{C}_2\text{H}_4\text{O})_2\text{C}_4\text{H}_9$	0.8853 <sub>20</sub> <sup>*</sup>	254.6			
<i>Aldehydes</i>						
Butyraldehyde	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	0.8016 <sub>20</sub> <sup>*</sup>	74.78	1.37911 <sub>20</sub> <sup>*</sup>	13.4	7.1% at 25°
<i>Ketones</i>						
Acetone	$\text{CH}_3\text{COCH}_3$	0.79079 <sub>20</sub> <sup>*</sup>	56.5	1.35886 <sub>19</sub> <sup>**</sup>	20.7	Completely soluble
2,4-Pentanedione (acetylacetone)	$\text{CH}_3\text{COCCH}_2\text{COCCH}_3$	0.9753	140.5	1.45178 <sub>18</sub> <sup>5*</sup>	25.7	Soluble in water acidified with HCl
2-Butanone (methyl ethyl ketone, MEK)	$\text{CH}_3\text{CH}_2\text{COCH}_3$	0.805 <sub>20</sub> <sup>*</sup>	79.6	1.38071 <sub>15</sub> <sup>9*</sup>	18.5	35.3% at 10°
2-Pentanone	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{CH}_3$	0.812 <sub>15</sub> <sup>*</sup>	101.7	1.38946 <sub>23</sub> <sup>**</sup>	15.4	Very slightly soluble
3-Pentanone	$(\text{C}_2\text{H}_5)_2\text{CO}$	0.80953 <sub>25</sub> <sup>*</sup>	101.70	1.39240 <sub>20</sub> <sup>*</sup>	17.0	4.7 g./100 ml. at 20°
4-Methyl-2-pentanone (hexanone, methyl isobutyl ketone, MIBK)	$\text{CH}_3\text{COCCH}_2(\text{CH}_2)_2$	0.815 <sub>15</sub> <sup>*</sup>	93	1.38788 <sub>16</sub> <sup>**</sup>		Very slightly soluble
2-Heptanone	$(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_3$	0.8006 <sub>20</sub> <sup>*</sup>	115.8	1.3959 <sub>20</sub> <sup>*</sup>	13.1	2 parts/100 parts at 20°
2,6-Dimethyl-4-heptanone (diisobutyl ketone)	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{CH}_3$	0.822 <sub>15</sub> <sup>*</sup>	150		11.9	Very slightly soluble
2,4-Dimethyl-3-pentanone (diisopropyl ketone)	$(\text{CH}_3)_2\text{CHCH}_2\text{COC}(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$	0.938	164-166	1.4300 <sub>1</sub> <sup>*</sup>		Soluble
Cyclohexanone	$[(\text{CH}_2)_5\text{CH}]_2\text{CO}$	0.8062 <sub>20</sub> <sup>*</sup>	123.7			Insoluble
	$(\text{CH}_2)_5\text{CO}$	0.95099 <sub>15</sub> <sup>*</sup>	156.7	1.45203 <sub>15</sub> <sup>*</sup>	18.3	5 g./100 ml. at 30°

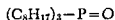


Mesityl oxide	0.8539 <sub>20</sub> <sup>o</sup>	128.7	1.446 <sub>16</sub> <sup>o</sup>	15.6	3 g./100 ml.
Isophorone	0.9229 <sub>20</sub> <sup>o</sup>	215.2			Slightly soluble
ESTERS					
Methyl acetate	0.9274 <sub>25</sub> <sup>o</sup>	57.1	1.36193 <sub>20</sub> <sup>o</sup>	6.7	31.9% at 20°
Ethyl acetate	0.901 <sub>20</sub> <sup>o</sup>	77.15	1.37216 <sub>18.9</sub> <sup>o</sup>	6.0	8.6% at 20°
n-Propyl acetate	0.8667 <sub>20</sub> <sup>o</sup>	101.6	1.38442 <sub>20</sub> <sup>o</sup>	5.7	1.89% at 20°
Isopropyl acetate	0.869 <sub>25</sub> <sup>o</sup>	89	1.37730 <sub>20</sub> <sup>o</sup>		3.09% at 20°
n-Butyl acetate	0.8813 <sub>20</sub> <sup>o</sup>	126.5	1.39406 <sub>20</sub> <sup>o</sup>	5.0	0.5% at 25°
2-Butyl acetate	0.8648 <sub>25</sub> <sup>o</sup>	112-113	1.3866 <sub>25</sub> <sup>o</sup>		3%
Isobutyl acetate	0.871 <sub>20</sub> <sup>o</sup>	116.5	1.39018 <sub>20</sub> <sup>o</sup>	5.3	0.63% at 25°
n-Amyl acetate	0.8753 <sub>20</sub> <sup>o</sup>	149.2	1.40228 <sub>20</sub> <sup>o</sup>	4.8	0.2 ml./100 ml. at 20°
Benzyl acetate	1.057 <sub>16</sub> <sup>o</sup>	215.0	1.5200 <sub>20</sub> <sup>o</sup>	5.1	Slightly soluble
Ethyl propionate	0.8846 <sub>25</sub> <sup>o</sup>	99.10	1.38394 <sub>20</sub> <sup>o</sup>	5.7	2% at 20°
Butyl propionate	0.8828 <sub>15</sub> <sup>o</sup>	145.4			Insoluble
Amyl propionate	0.870-0.873	140-170			0.1 ml./100 ml. at 20°
Butyl butyrate	0.870-0.880	160-165	1.4049 <sub>20</sub> <sup>o</sup>		Insoluble
Methyl benzoate	1.09334 <sub>15</sub> <sup>o</sup>	199.6	1.51810 <sub>16</sub> <sup>o</sup>	6.6	Insoluble
Ethyl benzoate	1.05112 <sub>15</sub> <sup>o</sup>	212.6	1.50748 <sub>15</sub> <sup>o</sup>	6.0	0.08 g./100 g. at 20°
Diethyl malonate	1.05496 <sub>20</sub> <sup>o</sup>	199.30	1.41363 <sub>20</sub> <sup>o</sup>	7.9	2.08 g./100 ml. at 20°
Diethyl oxalate	1.0785 <sub>20</sub> <sup>o</sup>	185.4	1.41239 <sub>15</sub> <sup>o</sup>	8.1	Slightly soluble
n-Butyl phosphate (tributyl phosphate)	0.9727 <sub>27</sub> <sup>o</sup>	177-178	1.4226 <sub>20</sub> <sup>o</sup>	8.0	0.6 parts/100 parts
		at 25 mm.			
		(decom-			
		poses at			
		289°)			
Ethyl acetoacetate	1.0250 <sub>20</sub> <sup>o</sup>	180-181		15.7	Slightly soluble
NITROGENOUS COMPOUNDS					
Diethylamine	0.7108 <sub>18</sub> <sup>o</sup>	55.5	1.38730 <sub>13</sub> <sup>o</sup>	3.6	Soluble
Dipropylamine	0.73400 <sub>20</sub> <sup>o</sup>	110.7	1.40455 <sub>19.5</sub> <sup>o</sup>	2.9	Soluble
Dibutylamine	0.7601 <sub>20</sub> <sup>o</sup>	159-161	1.41766 <sub>20</sub> <sup>o</sup>		Soluble
Diamylamine	0.77-0.78 <sub>20</sub> <sup>o</sup>	202-203	1.430 <sub>20</sub> <sup>o</sup>		Slightly soluble
		at 745 mm.			
Diethanolamine	1.0966 <sub>20</sub> <sup>o</sup>	269.1	1.4776 <sub>20</sub> <sup>o</sup>		Soluble
Dibenzylamine	1.026 <sub>22</sub> <sup>o</sup>	300.0	1.57432 <sub>22</sub> <sup>o</sup>	3.6	Insoluble
Pyridine	0.98783 <sub>15</sub> <sup>o</sup>	115.3	1.50919 <sub>21</sub> <sup>o</sup>	12.3	Soluble
Quinoline	1.095 <sub>20</sub> <sup>o</sup>	237.7	1.62450 <sub>24.9</sub> <sup>o</sup>	9.0	6 g./100 ml.

\* Table from Morrison, G. H., and Freiser, Henry, Solvent Extraction in Analytical Chemistry, John Wiley and Sons, Inc., 1957. Reprinted with permission.

in a benzene or xylene solution. It is only slightly soluble in water. In some cases it is used as the solvent also. The reagent extracts from strongly acidic solutions.

### TRI-*n*-OCTYLPHOSPHINE OXIDE



Tri-*n*-octylphosphine oxide (TOPO) is a white, waxy crystalline compound melting at 51 to 52°C. It is soluble in hydrocarbons, insoluble in water. Cyclohexane is often used as a solvent, although carbon tetrachloride is useful as a diluent when inversion of the phases is desired. The commercial product can generally be used without further purification.

Tri-*n*-octylphosphine oxide is most useful as an extractant from highly acidic solutions, in excess of 1 *M*. Highest extraction coefficients are achieved from acidic chloride and nitrate solutions. The addition of chloride or nitrate to sulfate or perchlorate solutions often leads to effective separations. Mineral acids are co-extracted to some extent.

## Chapter 8

# SEPARATIONS BY DISTILLATION AND EVAPORATION

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**Introduction.**—Separating elements through the vapor phase is less convenient than separating them by precipitation or solvent extraction, but it is usually clean and quantitative. The lighter elements are those most often separated by vaporization, especially the non-metals and pseudometals. The method can, however, be extended to a number of metals by using higher temperatures or reduced pressures.

Organic elementary analysis, the determination of carbon, hydrogen, nitrogen, and oxygen in organic compounds, requires the separation of these elements as gases. Carbon and hydrogen are burned to carbon dioxide and water, which are absorbed in weighed bulbs containing appropriate reagents. Nitrogen, in the Dumas method, is measured as nitrogen gas, while oxygen, in the Unterzaucher method, is converted to carbon monoxide, which reacts with iodine pentoxide to yield iodine vapor, which in turn is absorbed and determined by titration. Much experimental detail is involved in these methods, and one can profit by referring to textbooks on the subject.<sup>1</sup>

The conversion of oxygen to carbon monoxide is the basis of many "vacuum fusion" methods for determining oxygen in metals.<sup>2</sup> A newer method which is applicable to organic<sup>3</sup> as well as inorganic<sup>4</sup> compounds, is the reaction with  $\text{BrF}_3$  to yield gaseous oxygen.

The Kjeldahl method for determining nitrogen is well known.<sup>1</sup> Nitrogen in organic compounds is converted to ammonium sulfate by digesting with hot concentrated sulfuric acid and appropriate catalysts,<sup>5</sup> then ammonia gas is liberated by adding sodium hydroxide, is distilled and absorbed in boric acid or a measured volume of standard hydrochloric acid, then determined by titration. Nitrogen can readily be determined in nitrates by reducing these to ammonia in alkaline solution with Devarda alloy (Cu 50%, Al 45%, Zn 5%) and simultaneously removing the ammonia by distillation.

<sup>1</sup> Steyermark, A., *Quantitative Organic Microanalysis*, New York, The Blakiston Co., 1951.

<sup>2</sup> Booth, E., Bryant, F. J., and Parker, A., *Analyst*, **82**, 50, 1957; Bennett, S. J., and Covington, L. C., *Anal. Chem.*, **30**, 363, 1958.

<sup>3</sup> Shaft, I., and Katz, J. J., *Anal. Chem.*, **29**, 1322, 1957.

<sup>4</sup> Hockstra, H. R., and Katz, J. J., *Anal. Chem.*, **25**, 1608, 1953.

<sup>5</sup> Bradstreet, R. B., *Anal. Chem.*, **29**, 944, 1957; *Chem. Rev.*, **27**, 331, 1940.

## SEPARATION OF THE ELEMENTS

Our main concern in this chapter will be with elements other than the four just mentioned. We shall also ignore the inert gases. With these exceptions, those elements that are most often separated for analytical purposes by distillation or evaporation will be reviewed in approximate order of atomic number. We are primarily concerned with separation by vaporization as a prelude to, or a

part of, the analytical determination of the element that is vaporized. Vaporization, however, is also used to remove unwanted elements before determining other constituents, and vaporization may lead to unintentional losses, if an analyst is not aware of this possibility.

**Boron.**—There are few, if any, reactions specifically for borate in aqueous solutions. Except with the simplest of mixtures, it is necessary to separate borate from other constituents before it can be determined, and this is almost always done by distillation of the ester methyl borate,  $B(OCH_3)_3$ , b.p.  $68.5^\circ$ . The sample containing a soluble borate is placed in a distilling flask with a small amount of sulfuric or hydrochloric acid and a minimum of water; a considerable excess of methanol is added, and the liquid is distilled at  $75^\circ$  to  $80^\circ$ , keeping the volume constant by passing methanol vapor during the distillation, or by adding methanol directly through a funnel. Typical apparatus is shown in Figs. 8-1 and 8-2. The distillate is caught in dilute sodium hydroxide solution (0.1 to 0.5 N), which is later evaporated to small volume and acidified. The boric acid is either determined by titration with standard base, using mannitol to complex the boric acid,<sup>6</sup> or photometrically with curcumin or 1,1'-dianthrindim.<sup>7</sup>

Fig. 8-1. Spicer and Strickland Apparatus for Micro Distillation of Methyl Borate.

There are many modifications of the distillation procedure, depending on the nature of the sample and the quantity of boron. In one method,<sup>8</sup> for quantities up to 20 mg. (as in Fig. 8-1), the sample is placed in the distilling flask with a minimum of water. Then 5 ml. concentrated sulfuric acid is added; the solution is evaporated to fumes and cooled; and then 40 ml. methanol is added. This is distilled, and the distillate collected in aqueous sodium hydroxide; then more methanol is added and the distillation is repeated. At the other extreme, a method for microgram and submicrogram quantities has recently been described<sup>9</sup> in which perchloric acid is used to catalyze the esterification, and glycerol is added to the sodium hydroxide solution in the receiver to give better retention of boric acid. Special equipment and techniques for boron in sedimentary rocks,<sup>10</sup> glasses,<sup>11</sup> and fertilizers<sup>12</sup> are also described.

<sup>6</sup> Wilcox, L. V., *Ind. Eng. Chem., Anal. Ed.*, **2**, 358, 1930.

<sup>7</sup> Baron, H., *Z. anal. Chem.*, **143**, 339, 1954.

<sup>8</sup> Schulek, E., and Vastagh, G., *Z. anal. Chem.*, **84**, 167, 1931.

<sup>9</sup> Spicer, G. S., and Strickland, J. D. H., *Anal. Chim. Acta*, **18**, 523, 1958.

<sup>10</sup> Werner, H., *Z. anal. Chem.*, **168**, 266, 1959.

<sup>11</sup> Ehrlich, P., and Keil, T., *Z. anal. Chem.*, **165**, 188, 1959.

<sup>12</sup> Roth, H., and Beck, W., *Z. anal. Chem.*, **141**, 404, 1954.

The esterification of boric acid with methanol is more rapid than most esterifications, but is, nevertheless, slow enough so that extended or repeated distillation is needed to recover boric acid quantitatively. A certain amount of water is necessary, as completely anhydrous conditions are not desirable.

Complications arise when the sample contains much silica or more than a trace of fluorine. A preferable extraction technique may be one that separates microgram amounts of boron from gram amounts of silica.<sup>13</sup> Fluoride ions combine with borate to form the stable fluoborate ion. Fluoride interference can be prevented, however, by adding a large excess of a solution of anhydrous aluminum chloride in methanol before the distillation.<sup>14</sup> Fluoride is held as  $\text{AlF}_6^-$ . Vanadium, if present, distills with methyl borate, presumably as a methyl vanadate ester; preliminary separation is necessary.<sup>15</sup>

Borosilicate glass should not be used for methyl borate distillations. It is best to use a silica distilling flask and condenser, and a receiver of silica, platinum, or silver.

**Fluorine.**—Fluorine is an impediment to many analytical determinations, as it forms complex ions or sparingly soluble fluorides with many metals. It is easily

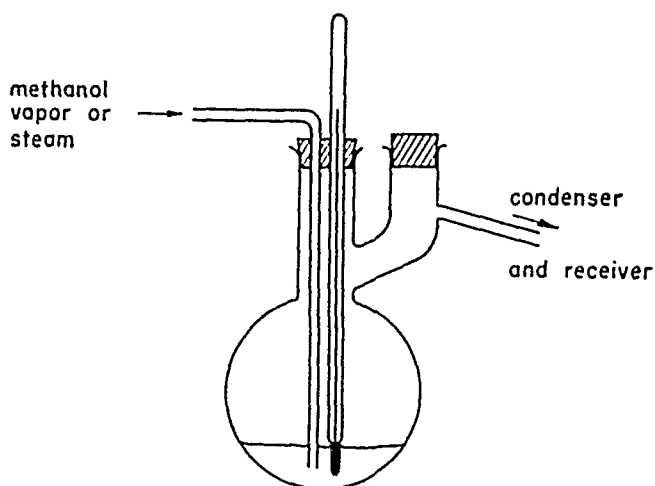


FIG. 8-2. Simple Apparatus for the Willard and Winter Distillation; Can Also Be Used for Methyl Borate. Steam Is Passed to Distil Fluosilicic Acid, Methanol to Distil Methyl Borate.

removed by evaporation with sulfuric or perchloric acid. Because of their very general reactivity with metal ions, fluoride ions must as a rule be separated from mixtures before they can be analytically determined. Separation is accomplished by distillation as fluosilicic acid,  $\text{H}_2\text{SiF}_6$ . The sample is placed in a distilling flask with glass beads or broken porous pot; sulfuric acid or perchloric acid is added, and the mixture is distilled, keeping the temperature about  $135^\circ$  to  $140^\circ$ . Under these conditions fluorine distills as  $\text{H}_2\text{SiF}_6$  rather than  $\text{SiF}_4$ , and there is evidence that some may distill as  $\text{HF}$ . As water boils out of the solution more is added, either through a funnel, or, more usually, by passing steam. The apparatus is similar to that shown in Fig. 8-2, with the addition of a thermometer to read the

<sup>13</sup> Pohl, F. A., *Z. anal. Chem.*, **157**, 6, 1957.

<sup>14</sup> Gaestel, C., and Huré, J., *Bull. Soc. Chim.*, **16**, 830, 1949.

<sup>15</sup> Weiss, G., and Blum, P., *Bull. Soc. Chim.*, **14**, 1077, 1947.

temperature of the contents of the distilling flask. The receiver contains water. About 100 ml. of distillate are collected for 10 mg. of fluorine.

The original distillation method of Willard and Winter<sup>16</sup> has been modified by various workers. Thus, a vapor jacket may be used to control the temperature of the distilling flask,<sup>17</sup> and phosphoric acid may be used in the flask in addition to perchloric.<sup>18</sup> One modification uses an aluminum chloride solution to receive the distillate.<sup>19</sup> Usually water is used in the receiver, and the distillate contains fluosilicic acid, hydrofluoric acid, and suspended silica. Fluosilicic acid hydrolyzes easily and is treated for analysis as though it were hydrofluoric acid. The fluoride is titrated with thorium nitrate using sodium alizarinsulfonate at pH 2.6 to 3.4,<sup>18,20</sup> or determined photometrically by the bleaching of the zirconium-alizarin<sup>21</sup> or thorium-thoron<sup>18</sup> lake.

Borosilicate glass may be used in the still; small amounts of boron in either the glass or the sample form  $\text{HBF}_4$ , but this does not interfere in the determination of fluorine. Much gelatinous silica retards distillation. More serious interference is given by aluminum. In the analysis of aluminosilicate rocks, one may fuse the rock with sodium carbonate plus zinc oxide, and extract the melt with water. Most of the aluminum remains in the insoluble residue, while the fluoride is in solution.<sup>18</sup> A method for determining fluorine in alumina ores and catalysts makes a preliminary separation by fusing the sample with potassium pyrosulfate in a quartz flask at 800°, blowing air through the melt to drive off HF, which is absorbed in aqueous sodium hydroxide, then separated again by a Willard and Winter distillation.<sup>20</sup> Yet another method uses hydrolysis of the sample by water vapor at 760° to liberate fluosilicic acid.<sup>22</sup>

**Silicon.**—Silicon is removed where it is unwanted, for example in the "opening-up" of silicate rocks or in the purification of hydrous oxide precipitates, which carry absorbed silica, by evaporating with hydrofluoric and sulfuric (or perchloric) acids in a platinum dish. The excess of hydrofluoric acid evaporates before the sulfuric acid or perchloric acid, so that the final residue is free from fluoride as well as silica. Where much silica has to be removed, a second or third evaporation can always be performed.

Certain elements may be lost as volatile fluorides during this evaporation. These include B, Ge, As, Sb, Se, and also the metals Cr, Mn and Re.<sup>23</sup>

Where fluoride is present in a sample, the volatility of fluosilicic acid interferes with the quantitative precipitation of silica by evaporation with perchloric or hydrochloric acid, unless steps are taken to prevent loss. By adding excess boric acid the fluoride is vaporized as  $\text{BF}_3$  and the silica recovered quantitatively.<sup>24</sup>

**Sulfur.**—Where it is necessary to determine sulfur in the sulfide form, as distinct from total sulfur, the sample is treated with hydrochloric acid and the liberated hydrogen sulfide gas is absorbed in ammoniacal zinc sulfate solution. It is then titrated with standard iodine solution following acidification. This method is mainly used in steel analysis.

<sup>16</sup> Willard, H. H., and Winter, O. B., *Ind. Eng. Chem., Anal. Ed.*, 5, 7, 1933.

<sup>17</sup> Huckaby, W. B., Welch, E. T., and Mettler, A. V., *Ind. Eng. Chem., Anal. Ed.*, 19, 154, 1947; Samachson, J., Slovik, N., and Sobel, A. E., *Anal. Chem.*, 29, 1888, 1957.

<sup>18</sup> Grimaldi, F. S., Ingram, B., and Cuttitta, F., *Anal. Chem.*, 27, 918, 1955.

<sup>19</sup> Balczó, H., Doppler, G., and Lanik, A., *Mikrochim. Acta*, 809, 1957.

<sup>20</sup> Abrahamczik, E., and Merz, W., *Mikrochim. Acta*, 445, 1959.

<sup>21</sup> Sanchis, J. M., *Ind. Eng. Chem., Anal. Ed.*, 6, 134, 1934.

<sup>22</sup> Gamble, L. W., Price, W. E., and Jones, W. H., *Anal. Chem.*, 32, 189, 1960.

<sup>23</sup> Chapman, F. W., Marvin, G. G., and Tyree, S. Y., *Anal. Chem.*, 21, 700, 1919.

<sup>24</sup> Schrenk, W. T., and Ode, W. H., *Ind. Eng. Chem., Anal. Ed.*, 1, 201, 1929.



**Chromium.**—For the determination of chromium itself it is seldom necessary to separate it from accompanying materials. There are, however, often occasions where chromium interferes in the determination of other metals. It may be removed by evaporation as chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ . The solution is evaporated to fumes with perchloric acid, then small amounts of powdered sodium chloride are added to the boiling solution until no more orange-red vapor is evolved and the color of the solution shows that the chromium has been removed. Or, hydrogen chloride gas can be passed over the boiling solution; this method has been applied to the analysis of corrosion-resistant steels<sup>25</sup> and low-grade uranium ores.<sup>26</sup>

In determining chromium itself, it is common to dissolve the sample in hydrochloric acid, then evaporate to fumes with perchloric acid in order to oxidize the chromium to chromic acid. Caution is indicated to avoid loss of chromyl chloride in such procedures.

**Germanium.**—Germanium tetrachloride,  $\text{GeCl}_4$ , boils at  $84^\circ$ , and is sufficiently stable towards water that it can be distilled from aqueous hydrochloric acid solution. In fact, germanium is easily lost from hydrochloric acid solutions, even at room temperature. The optimum concentration for distillation is 3 to 4 *N*,<sup>27</sup> but it is best to continue distillation until constant-boiling hydrochloric acid forms, or else some of the germanium may stick to the walls of the condenser.<sup>28</sup> Tin does not distil under these conditions; it stays in solution as the stable ion,  $\text{SnCl}_6^-$ . Antimony and selenium do not distil in significant amounts; arsenic forms volatile  $\text{AsCl}_3$ , but if a current of chlorine is passed to keep arsenic in the pentavalent form, the vaporization of arsenic is prevented.

Where a little arsenic has to be separated from much germanium, as in the analysis of semiconductors, a solvent extraction method is best.<sup>29</sup>

**Arsenic, Antimony, and Tin.**—As indicated above, arsenic can be distilled from 6 *N* hydrochloric acid at  $110^\circ$  to  $112^\circ$  as long as it is in the trivalent form. It may be carried over quantitatively as  $\text{AsCl}_3$  in a stream of carbon dioxide,<sup>30</sup> and separated completely from much larger amounts of tin and antimony.<sup>31</sup> By changing the conditions it is possible to distil arsenic, antimony, and tin successively in the same apparatus.<sup>32</sup> After arsenic has distilled, phosphoric acid is added to complex the tin and raise the boiling point; the temperature is raised to  $160^\circ$ , and concentrated hydrochloric acid is dropped slowly into the flask. Antimony is distilled as  $\text{SbCl}_3$  (b.p.  $219^\circ$ ). Finally, tin is distilled as a mixture of  $\text{SnCl}_4$  (b.p.  $113^\circ$ ) and  $\text{SnBr}_4$  by adding a mixture of hydrochloric and hydrobromic acids, 3:1 by volume, and distilling at  $140^\circ$ .

Arsenic is readily distilled from hydrobromic acid solutions, and this method has been favored for determination of trace concentrations. In a well-known method for arsenic in biological materials,<sup>33</sup> the sample is digested with sulfuric, nitric, and perchloric acids, then transferred to the distilling flask where the nitric

<sup>25</sup> Bricker, L. G., Weinberg, S., and Proctor, K. L., *Ind. Eng. Chem., Anal. Ed.*, **17**, 661, 1945.

<sup>26</sup> Sill, C. W., and Peterson, H. E., *Anal. Chem.*, **24**, 1175, 1952.

<sup>27</sup> Geilmann, W., and Brunger, K., *Z. anorg. Chem.*, **196**, 312, 1931.

<sup>28</sup> Harris, P. G., *Anal. Chem.*, **26**, 737, 1954.

<sup>29</sup> Luke, C. L., and Campbell, M., *Anal. Chem.*, **25**, 1588, 1953; *ibid.*, **28**, 1273.

<sup>30</sup> Rodden, C. J., *J. Research Nat. Bur. Standards*, **24**, 7, 1940.

<sup>31</sup> Coppins, W. C., and Price, J. W., *Metallurgia*, **46**, 52, 1952; *Chem. Abstracts*, **46**, 9462h, 1952.

<sup>32</sup> Scherrer, J. A., *J. Research Nat. Bur. Standards*, **16**, 253, 1936; *ibid.*, **21**, 95, 1938.

<sup>33</sup> Magnuson, H. J., and Watson, E. B., *Ind. Eng. Chem., Anal. Ed.*, **16**, 339, 1944.

acid is removed by boiling. Concentrated potassium bromide solution is then added. Arsenic distills rapidly, apparently as a pentabromide, since the distillate (collected in water) contains arsenic wholly as arsenate. In this form it is ready, without further oxidation, to be determined by the molybdenum blue method. Ammonium molybdate is added, then hydrazine, to reduce the arsenomolybdate to molybdenum blue. This is determined photometrically. For most accuracy in the microgram range the acidity of the distillate must be adjusted before adding ammonium molybdate.<sup>34</sup>

Arsenic is also separated as arsine,  $\text{AsH}_3$ . This is formed quantitatively over a wide range of conditions by reduction of arsenic-containing solutions with zinc and sulfuric acid. It may be absorbed in dilute iodine solution and converted to arsenate for determination as molybdenum blue,<sup>35</sup> or it can be absorbed in mercuric chloride solution, again with a molybdenum blue finish.<sup>36</sup> In the classical Gutzeit method, the arsine, carried by hydrogen, passes over a strip of paper impregnated with mercuric chloride and stains it yellow or black according to the amount of arsenic present.

**Selenium.**—Selenium is distilled as the tetrabromide under oxidizing conditions. Soils, for example,<sup>37</sup> are dried and placed in a distilling flask with a sufficient quantity of a mixture of concentrated hydrobromic acid and bromine (10:1 by volume) to give a permanent bromine color. More hydrobromic acid is added and the mixture distilled. A little hydrobromic acid-bromine mixture is first placed in the receiver. Organic matter can be ashed with nitric, sulfuric, and perchloric acids without loss of selenium; the product of the ashing is distilled with hydrobromic acid and bromine plus additional sulfuric acid.<sup>38</sup> A simple distillation technique has been devised for field use in geochemical prospecting; 1 g. of rock or soil is mixed with 2 ml. sulfuric acid and 5 ml.  $\text{HBr-Br}_2$  mixture, and distilled. The still is simply a micro-Kjeldahl flask with its neck bent over. To avoid carrying liquid bromine, bromine is liberated *in situ* by adding potassium bromate to the hydrobromic acid. The first 4 ml. of distillate contains virtually all the selenium.<sup>39</sup>

The selenium in the distillate is generally reduced to elemental selenium by sulfur dioxide, hydroxylamine, or ascorbic acid. The selenium is filtered and weighed, or, more often, estimated by its red color. Microgram amounts of selenium can be determined photometrically by the reaction of selenious acid with diaminobenzidine.<sup>40</sup>

**Osmium.**—Compounds of osmium are readily oxidized to  $\text{OsO}_4$ , (b.p.  $129^\circ$ ). Osmium is thus easily separated from the other platinum metals. The vapor of  $\text{OsO}_4$  can be distilled from aqueous solutions.

In the classical procedure of Gilchrist,<sup>41</sup> the sample is treated in the distilling flask with 1:1 nitric acid and a slow stream of air passed through the boiling solution to carry away the osmium tetroxide. A better oxidizing agent, particularly if

<sup>34</sup> Hoffman, I., and Rowsome, M., *Analyst*, **85**, 151, 1960.

<sup>35</sup> Kingsley, G. R., and Schaffert, R. R., *Anal. Chem.*, **23**, 914, 1951.

<sup>36</sup> Nazarenko, V. A., Ilyantikova, G. F., and Lebedeva, N. B., *Zavod. Lab.*, **23**, 891, 1947; *Anal. Abstracts*, **5**, 2954, 1958.

<sup>37</sup> Robinson, W. O., Dudley, H. C., Williams, K. T., and Byers, H. G., *Ind. Eng. Chem., Anal. Ed.*, **6**, 274, 1934.

<sup>38</sup> Fogg, D. N., and Wilkinson, N. T., *Analyst*, **81**, 525, 1956.

<sup>39</sup> Lakin, H. W., *Proceedings of XX. International Geological Congress, Mexico City*, 1956.

<sup>40</sup> Hoste, J., and Gillis, J., *Anal. Chim. Acta*, **12**, 158, 1955.

<sup>41</sup> Gilchrist, R., *J. Research Nat. Bur. Standards*, **6**, 421, 1931.

chloro-complexes of osmium are present, is boiling perchloric acid.<sup>42</sup> The osmium tetroxide is absorbed in 6 *N* hydrochloric acid saturated with sulfur dioxide. The absorption is somewhat slow, and at least two traps should be used in series. The final determination is done gravimetrically as osmium metal<sup>41</sup> or photometrically with thiourea.<sup>13</sup>

**Mercury.**—Mercury metal is easily liberated from its compounds by heating them with calcium carbonate or sodium carbonate in air, or with an oxidizing agent. It may also be vaporized from aqueous solutions as  $\text{HgCl}_2$ . Mercury can be determined in organic compounds by ashing them in the distilling flask with fuming sulfuric acid and ammonium persulfate (perchloric acid may also be used), and then passing hydrogen chloride gas and raising the temperature. Mercuric chloride distills quantitatively and may be determined in the distillate by precipitation of  $\text{ZnHg}(\text{SCN})_4$ .<sup>44</sup>

## EVAPORATION OF METALS AT HIGH TEMPERATURES

Metals vary greatly in their boiling points, as the following table shows:

<i>Metal</i>	<i>B.p. at 760 mm.</i>	<i>Metal</i>	<i>B.p. at 760 mm.</i>
Cd	767	Al	2056
Zn	906	Sn	2260
Mg	1100	Cu	2310
Bi	1560		
Pb	1750		
Ag	1927		

By distilling at low pressures the temperatures needed are reduced, and differences in vapor pressure are magnified. A large difference in boiling point between two metals does not necessarily imply efficient separation, however. Little is known of vapor pressure-composition relations for mixtures of metals,<sup>45</sup> and the techniques of fractional distillation commonly used at lower temperatures are impractical here. Distillations are made with "one theoretical plate." Techniques are described for rapid analysis of alloys by heating weighed samples in silica vessels to temperatures of 800° to 1000° and pressures down to 10<sup>-4</sup> mm.<sup>46, 47</sup> and either measuring the decrease in weight as one metal is vaporized and another left behind, or noting visually the density of the mirrors produced as one metal after another deposits on the walls of the tube beyond the heated portion.<sup>47</sup> Certain sulfides can be vaporized and separated by this last technique.<sup>47</sup>

Evaporation in a stream of nitrogen has been used to extract traces of lead from iron and stone meteorites in geochemical research.<sup>48</sup> Charges weighing up to 25 g.

<sup>42</sup> Westland, A. D., and Beamish, F. E., *Anal. Chem.*, **26**, 739, 1954.

<sup>43</sup> Allen, W. J., and Beamish, F. E., *Anal. Chem.*, **24**, 1608, 1952.

<sup>44</sup> Fenimore, E. P., and Wagner, E. C., *J. Am. Chem. Soc.*, **53**, 2468, 1931.

<sup>45</sup> Leitgeb, W., *Z. anorg. Chem.*, **302**, 305, 1931.

<sup>46</sup> Bogdandy, St. v., and Polanyi, M., *Metal Industries*, **31**, 195, 1927; Töpelman, H., in Böttger, W., (ed.), *Physikalische Methoden der analytischen Chemie*, III, Akademische Verlagsgesellschaft, Leipzig, **74**, 1939; Colbeck, E. W., Craven, S. W., and Murray, W., *Analyst*, **59**, 395, 1934.

<sup>47</sup> Jungbühnel, G., *Chem. Technik*, **8**, 588, 1956.

<sup>48</sup> Marshall, R. R., and Hess, D. C., *Anal. Chem.*, **32**, 960, 1960.

are placed in a graphite crucible inside a quartz tube and heated by an induction furnace to 1400°; see Fig. 8-3. Lead is vaporized and condensed in moist quartz wool, then dissolved in acid, purified by a dithizone extraction, and transferred to the filament of a mass-spectrometer for isotopic analysis.

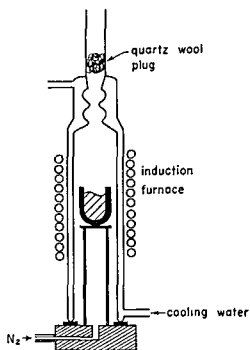


FIG. 8-3. Distilling Apparatus for Recovering Microgram Quantities of Lead from Meteorites and Silicate Rocks.<sup>49</sup>

A somewhat similar technique has been used to separate traces of zinc from bauxite, clays, and oxide minerals,<sup>50</sup> and from pyrites.<sup>51</sup> The samples are placed in a ceramic boat in a quartz tube, and heated in a furnace at 1100° for 30 to 60 minutes. Silicate materials are mixed beforehand with carbon and magnesium oxide; pyrite is mixed with carbon and powdered iron. A stream of hydrogen is passed during ignition; see Fig. 8-4. Zinc condenses in the narrow part of the tube just outside the furnace. It is not pure, but may contain Cd, Pb, Bi, Sb, As, Ge, and Tl if these were present in the original sample. The metal mirror is dissolved in hydrochloric acid and the zinc determined polarographically or with dithizone, using masking agents to prevent interference from the impurities. If major amounts of lead and other volatile metals are present, more elaborate separation procedures are needed,

and there is then little point in using the vaporization procedure in preference to other methods. The advantage of the vaporization method, where it can be

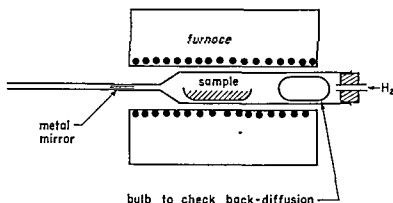


FIG. 8-4. Distilling Apparatus for Recovering Zinc and Other Metals from Clays.

applied, is its speed and simplicity, and the fact that few reagents are required, which is an important consideration in trace analysis.

<sup>49</sup> Edwards, G., and Urey, H. C., *Geochim. et Cosmochim. Acta*, 7, 154, 1955.

<sup>50</sup> Geilmann, W., and Neeb, R., *Angew. Chem.*, 67, 26, 1955.

<sup>51</sup> Geilmann, W., Neeb, R., and Eschnauer, H., *Z. anal. Chem.*, 154, 418, 1957.

## APPARATUS FOR FRACTIONAL DISTILLATION

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A very inexpensive type of fractionation apparatus that can satisfactorily meet many requirements for analytical distillation is shown in Fig. 8-5. The main parts are an ordinary boiling flask (100 ml. to 12 l.) and a 1- or 1.5-inch diameter pyrex

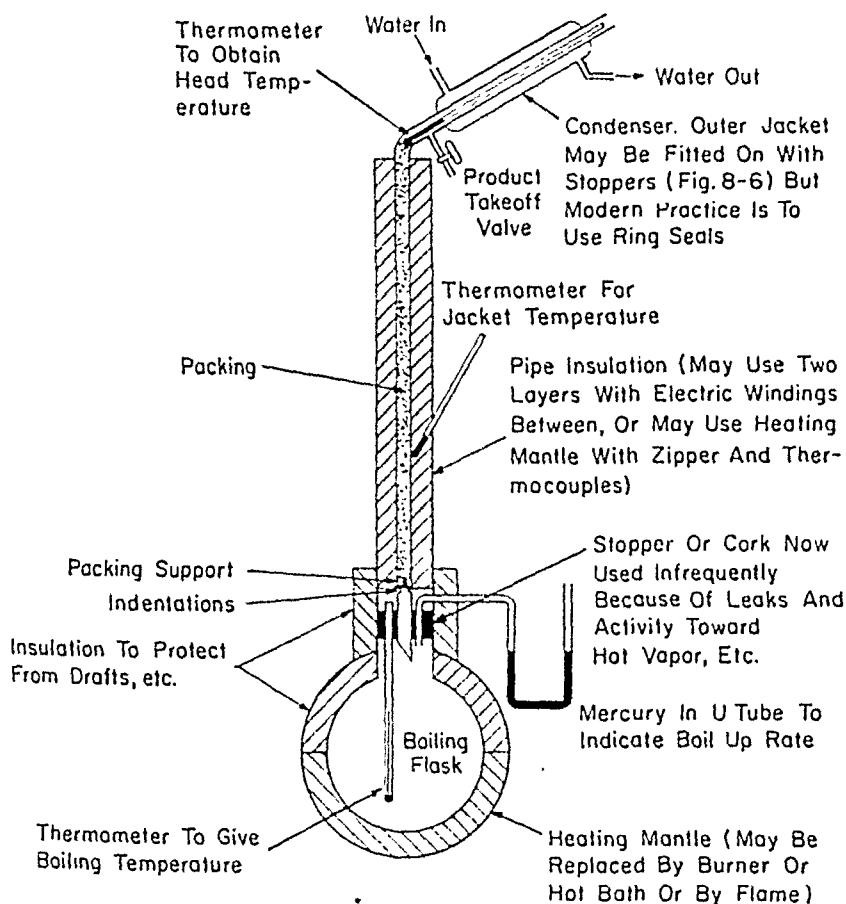


FIG. 8-5. Fractionation Apparatus.

tube bent to a 45° angle about 24 inches from one end. The long end of the tube, the fractionating column, is connected to the boiling flask by a rubber stopper, treated cork, or spherical glass connection. The boiling flask may be heated by a flame, a heating mantle, or a liquid bath. If a stopper or cork is used to connect the flask to the column, there should be extra holes for a thermometer and a manometer. The latter consists of a 6 mm. tube connected with one arm of a U-tube gauge containing mercury, whose reading indicates the back pressure in the boiling flask, and, therefore, gives a rough indication of the boilup rate.

Before connecting the fractionating column to the boiling flask it should be

fitted with a condenser, takeoff valve, packing, packing support, and insulation. It is also necessary to fit the rubber stopper or cork to the bottom end of the column, or to have the desired male spherical joint sealed onto the tube. When the spherical joint is used, the boiling flask should have a side arm for connection to the back pressure manometer, and a well for the thermometer. The most satis-

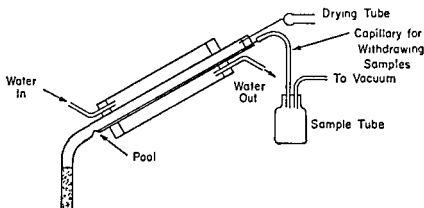


FIG. 8-6. Inexpensive Condenser.

factory condenser arrangement is achieved by ring sealing an outer jacket with water inlet and outlet onto the upper end of the main column tube. A very inexpensive condenser (Fig. 8-6) can be fitted to the upper end of the column by slipping a rubber stopper down over the tube until it is about three inches from the bend. A second hole in this stopper should be fitted with a 6-mm. glass tube to which the incoming water line may be connected. The outer jacket of the condenser is next slipped over the column tube, and then a second stopper is slipped down until it completes the assembly of the condenser jacket. The second stopper must be fitted with a 6-mm. tube to provide the water outlet.

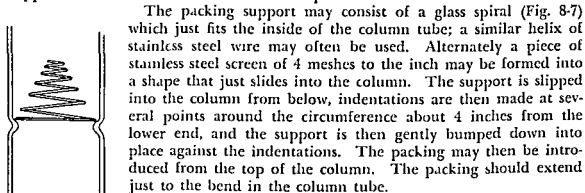


FIG. 8-7. Packing Support.

The packing support may consist of a glass spiral (Fig. 8-7) which just fits the inside of the column tube; a similar helix of stainless steel wire may often be used. Alternately a piece of stainless steel screen of 4 meshes to the inch may be formed into a shape that just slides into the column. The support is slipped into the column from below, indentations are then made at several points around the circumference about 4 inches from the lower end, and the support is then gently bumped down into place against the indentations. The packing may then be introduced from the top of the column. The packing should extend just to the bend in the column tube.

The least expensive kind of column can be insulated with a piece of steam pipe insulation, preferably the magnesia type, but any type will be fairly effective. An additional piece of such lagging, of larger diameter, should be used to insulate the section from the top of the still pot to the bottom of the column. Some similar arrangement of asbestos paper should be used to insulate the flask itself from variations in room conditions. At least one thermometer should be imbedded in the insulation, with the thermometer bulb firmly against the glass.

Product removal may be achieved by sealing a side arm with stopcock to the underside of the column tube just above the bend and just below the condenser. This becomes the most fragile part of the apparatus. An alternate (Fig. 8-6) is to

indent the bottom side of the column tube at the point between the condenser and bend, so that a small pool of product liquid collects at this point during column operation. A fine capillary is then passed in from the upper end of the column tube and fitted so that the lower end of the capillary will be submerged in the pool of liquid just below the condenser. The upper end of the capillary is passed through one hole of a two hole rubber stopper which is inserted into the upper end of the column tube. The second hole of this stopper must be open to the atmosphere, in some cases through a drying tube. The capillary line leads to a fraction collection test tube or bottle which may be evacuated at a controlled rate, so that the product is withdrawn from the product pool through the capillary and into the collection tube. These tubes should be easily removable so that a new tube can be substituted quickly when it is desired to start collecting a new fraction.

A vertical rod  $\frac{3}{8}$  inch in diameter, fastened firmly to the floor and wall, or otherwise firmly secured, should be used to support the column and flask, by means of suitable laboratory clamps. Similar rods and clamps should be used to support the product sample tubes, and other auxiliaries.

It is necessary to be able to estimate the temperature at the top of the packing. This may be done by passing a thermometer down from the upper end of the column tube until the thermometer bulb just touches the upper surface of the packing at a point removed from the outside walls of the column tube.

In most present day apparatus, a heating mantle is used to heat the boiling flask, and other mantles often serve to insulate the column proper as well as the connecting section between column and boiler. An offset condenser is provided (Fig. 8-8), and fitted with a reflux splitter controlled by a timing device. A well is provided for a thermometer or thermocouple, and other thermocouples provide means of measuring jacket and still pot temperatures.

Most analytical distillation can be done satisfactorily with any of the commonly available packings. If the material being distilled is inert to stainless steel, protruded metal packing is almost universally satisfactory as to separating power and throughput with freedom from flooding. If stainless steel cannot be tolerated, glass Raschig rings (length equal to diameter, about  $\frac{3}{16}$  inch) are satisfactory, or  $\frac{1}{4}$  inch glass helices with two turns each, may be used. Single turn helices, especially the small sizes, are prone to flooding except in the hands of experts.

For small samples, special equipment or suitable commercially available equipment is recommended.

For vacuum distillation, the various joints should be equipped with oil seals, and an open type of packing should be used unless very slow boilup can be tolerated and the operator is skilled and experienced.

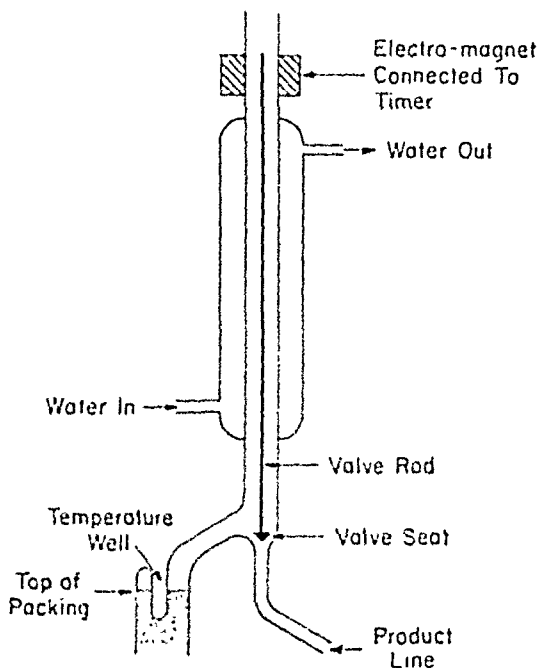


FIG. 8-8. Offset Condenser.

## Chapter 9

# CHROMATOGRAPHY

By Eugene W. Berg

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### INTRODUCTION

Chromatography has been defined as "the study and the utilization of widely applicable, analytical procedures for the resolution of mixtures of solutes by differential migration from a narrow zone in porous media, the migration being produced by electrical potential or by flow of liquid or gas."<sup>1</sup> Inherent with this definition is the concept of a driving and resistive force, either or both of which must act selectively on the solutes if they are to migrate at different rates. Thus, if the solvent flow or electrostatic potential gradient drives all particles uniformly, different migration rates must be established by selective resistive forces and vice versa. The more common resistive forces are viscosity, permeability, and adsorption processes, the latter being one of the most selective phenomena known to man, and one which tends to characterize most chromatography procedures.

*Technique of Chromatography.*—The technique of chromatography consists, in general, of percolating a homogeneous phase containing the sample mixture through another phase that is stationary and has a very large surface area. In practice, the percolating phase is a liquid or a gas, and the stationary phase is a column of porous solid adsorbent or a liquid phase immobilized by being adsorbed on a suitable solid adsorbent. As the solution percolates through the bed of adsorbent, a dynamic reversible equilibrium involving solute, solvent, and adsorbent is established. Solute particles compete with solvent particles as they strive to occupy the surface of the adsorbent; the more strongly the solvent is adsorbed, the greater the competition for adsorption of the solute. Hence, the solute spends a greater portion of the time in the solution phase and is carried along more rapidly by the solvent flow. The difference in adsorption affinities of otherwise similar substances causes the various solutes to migrate through the adsorption medium at characteristic rates and results in the separation of solutes. The sequence of solute zones, which develop in the adsorbent bed or in the effluent from the adsorbent bed, is termed a chromatogram.

Although there are various combinations of percolating and stationary phases and driving and resistive forces that can produce a differential migration of solutes, one cannot predict accurately what combination of components will pro-

<sup>1</sup> Strain, H. H., Sato, T. R., and Engelke, J., *Anal. Chem.*, 26, 95, 1954.



duce a suitable chromatogram. Chromatography is not on a rational theoretical basis yet; the field is empirical, and one must, therefore, rely heavily on experience. There is, however, much that is common to all chromatographic procedures.

The factors that determine separation efficiency are the same regardless of how the migration is produced or what media are used. As in all differential migration methods of separation, the narrower the zone from which migration originates, the shorter the distance the solutes must travel to be resolved. Similarly, the greater the difference of solute migration rates, the shorter the migration path needed for a resolution. Flow rates must be slow enough for equilibria to be established, and solute concentrations must be small because of the limited adsorbent surface available for adsorption. These concepts should be kept in mind when considering chromatographic separations because system variables are usually altered to enhance or suppress one of the above factors.

*Methods of Operating a Chromatographic Column.*—There are three ways of operating a chromatographic column: frontal analysis; displacement analysis; and elution analysis. Each method gives some unique information about the sample.

*Frontal Analysis.*—This is the simplest form of chromatography, and is best described as the continuous addition of the original sample solution to a column of adsorbent. A plot of the concentration of the solutes in the effluent of the column as a function of the volume of effluent is given in Fig. 9-1. The results are interpreted in the following manner. The solute *A*, with the least affinity for the

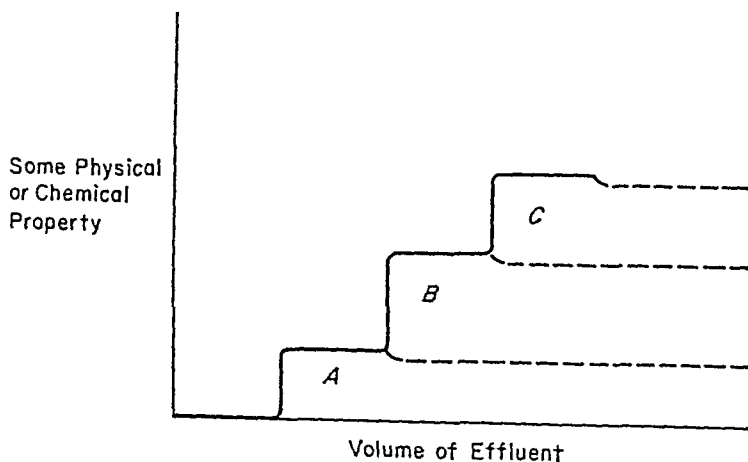


FIG. 9-1. A Typical Elution Pattern Obtained by Frontal Analysis.

adsorbent, will migrate through the column rapidly and appear in the effluent first. Solute *B*, with a slightly greater adsorption affinity, will appear in the effluent next, etc. One step will appear in the elution curve for each solute that appears in the effluent. The column effluent will be a mixture of solutes after the second component appears, and will increase in complexity with the appearance of each new solute until the effluent composition is identical to the influent. The number of steps in the elution curve designates only the minimum number of sample components. Frontal analysis is not effective for resolving mixtures, because only a limited portion of the least strongly adsorbed solute can be isolated in a pure form; it has the advantage, however, that irreversibly adsorbed solutes appear in the effluent.

**Displacement Analysis.**—In this method the sample solutes are adsorbed from a small volume of sample near the top of the adsorbent column and washed through the column with a solution or solvent having a greater affinity for the adsorbent than any of the sample components. As the developing solvent flows through the column it displaces all of the adsorbed solutes, which in turn displace each other. If the column is long enough for equilibrium to be approached, each component will move through the column as a zone of pure material. The least strongly adsorbed solute will appear in the effluent first, followed by other sample components in the order of increasing adsorption affinity. Finally, the displacing substance will appear in the effluent. A typical elution curve for displacement analysis is given in Fig. 9-2. Under equilibrium or near equilibrium conditions, all

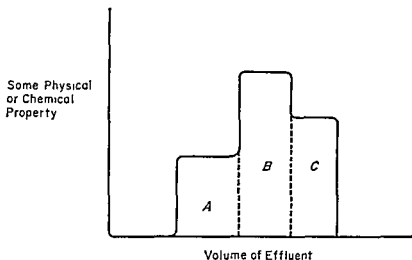


FIG. 9-2. A Typical Elution Pattern Obtained by Displacement Analysis.

solute zones move through the column at the same rate as the developer, but they are not completely resolved; the trailing edge of one zone will overlap the leading edge of the following zone. The method is theoretically limited to reversible adsorption systems because irreversibly adsorbed components will not appear in the effluent. The minimum number of sample components can be determined from the number of steps in the curve, and each component can be separated in a pure form, but not quantitatively. The method can be used for quantitative determinations, however, since only a given amount of solute can be adsorbed per unit weight of adsorbent. Thus, as the concentration of a sample component is increased, the length of the corresponding step in the elution curve is lengthened proportionately. Quantitative determinations are effected by comparing the volume of effluent required for the collection of a given component with a series of standard samples.

**Elution Analysis.**—This method is distinguished from the other techniques by the fact that the sample components are adsorbed from a small volume of sample solution near the top of the column, and then washed through the column with pure solvent. Each component will migrate through the column at a characteristic rate depending on its adsorption affinity. The result is that complex mixtures can conceivably be resolved completely. As in displacement analysis, elution analysis is applicable to reversibly adsorbed components only. Figure 9-3 shows a typical

elution curve for elution analysis. It is possible to determine the minimum number of sample components from the elution curve and to quantitatively resolve all components. Conventional qualitative and quantitative tests can be applied to the individual effluent fractions. The greater versatility of elution analysis is responsible for its being the most widely used form of chromatography.

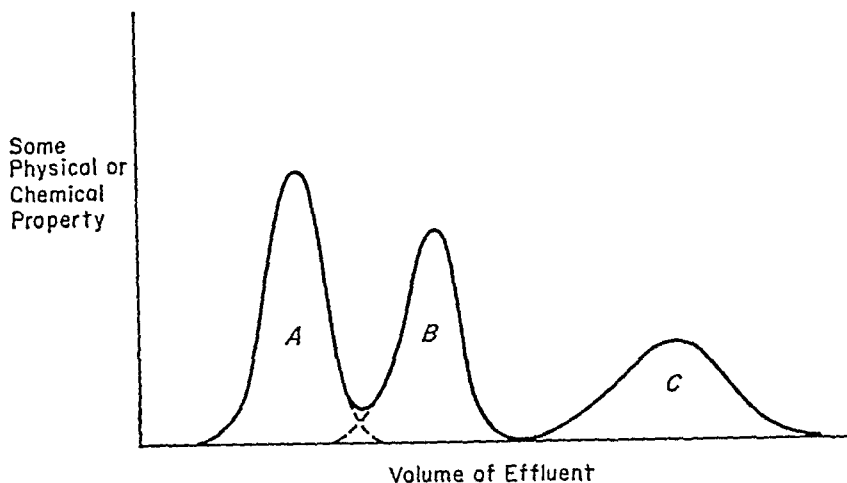


FIG. 9-3. A Typical Elution Pattern Obtained by Elution Analysis.

**The  $R_f$  Value.**—One of the most convenient means of presenting chromatographic data is to express the relative migration rates of the solutes as an  $R_f$  value, where

$$R_f = \frac{\text{distance traversed by leading edge of the solute zone}}{\text{distance traversed by leading edge of the solvent zone}}$$

$R_f$  values are a measure of the interaction of solute, solvent, and adsorbent, and are reproducible and characteristic for each solute in a given solvent-adsorbent system under specified conditions. The complete description of a chromatogram must include the  $R_f$  values of each solute, the description of solvent and adsorbent, and the system variables, such as temperature, flow rate, and solute concentrations.

**Recovery of Sample Components.**—Resolved sample components can be recovered in two ways. In the first method, each solute can be isolated in a single fraction or in a series of fractions as it appears in the effluent of the column, and then recovered by removing the solvent. The second method involves mechanically dividing the adsorbent column into fractions containing the individual solutes after the chromatogram has been developed. The solute can be eluted from the adsorbent and recovered by elimination of the solvent. The first technique is usually the more convenient to use.

**Application of Chromatography to Chemical Analysis.**—Due to its remarkable selectivity, chromatography has been used for qualitative and quantitative analysis, the resolution of mixtures, and concentration of dilute solutions. Qualitative tests are effected either by a direct comparison of  $R_f$  values for known and unknown, chromatographed under identical conditions, or by the use of a "mixed chromatogram." In the former instance, the criterion for solute identification is the development of a chromatogram identical to the known. In the latter instance, the

substance to be identified is mixed with pure material thought to be the same substance. If a single well-defined zone results when the mixture is chromatographed on two or three different adsorbents, the identity of the unknown is verified. The method is analogous to a mixed melting point determination, and is highly reliable. In fact, many researchers suggest that chromatographic homogeneity, especially in gas chromatography, is the most infallible criterion of purity that can be applied to a substance. A remarkable adjunct to qualitative tests is the application of identifying reactions, namely color producing reactions, to the developed chromatogram to confirm the presence or absence of a given solute or group of solutes.

Quantitative tests are generally applied to the resolved components only, and are more or less the classical quantitative procedures adapted to suit the analysis of solutes in the column effluent or on the adsorbent. Solutes can be concentrated on active adsorbents from dilute solutions, and recovered in a smaller solution volume by eluting the solute from the adsorbent with a more strongly adsorbed solvent.

The greatest application of chromatography has been the resolution of complex mixtures for subsequent qualitative or quantitative tests or for preparative work. Without the isolation by chromatographic procedures of the various plant pigments, vitamins, viruses, hormones, and metabolism products, it would have been impossible for our knowledge in these areas to develop as rapidly as it did. Possibly no other separation technique has exerted so great an influence on organic chemistry and biochemistry as has chromatography. Chromatography's influence on the field of inorganic chemistry has been much less spectacular but, even so, there are thousands of publications relating chromatography to inorganic analyses.

## ADSORPTION CHROMATOGRAPHY

Adsorption chromatography is characterized by the passage of the sample solution through a column of powdered or granular adsorbent.

**Adsorbents.**—The adsorbents should be insoluble and chemically inert under experimental conditions, preferably white or light colored, economical, convenient to use, and reproducible. Two conflicting factors, particle size and adsorbent surface area, must be considered. The capacity of a given adsorbent is inherently small but directly proportional to the surface area of the adsorbent and inversely proportional to the particle size. Every effort must be made to provide a large adsorbing surface but practical considerations make it necessary to use large enough particles so that column flow rates are reasonable. The compromise on particle size seems to cover the range from 100 to 300 mesh size. Even so, the smaller mesh sizes give such slow flow rates that a filter aid is required. Diatomaceous earths, kieselguhr, and certain forms of silica are excellent filter aids. When mixed with a stronger adsorbent they act as an inert diluent and increase the porosity of the adsorbent bed. Weight ratios as high as 1:1 are common.

The common adsorbents are, almost without exception, oxygen-containing organic or inorganic compounds, which are hydrophilic and have a high capacity for adsorbing water and only a slight tendency to adsorb nonpolar substances. The adsorbents are not alike in activity or capacity, but generally, solutes are adsorbed in the same sequence on different adsorbents. Some of the more common adsorbents are listed in Table 9-1 in the order of increasing strength of adsorp-

tion. The relative positions of the adsorbents in the table are for the activated forms and can be changed by deactivation. Dehydration and deactivation are usually synonymous terms when referring to adsorbents.

TABLE 9-1. COMMON HYDROPHILIC ADSORBENTS LISTED IN ORDER OF INCREASING STRENGTH OF ADSORPTION

Sucrose	Calcium phosphate
Cellulose	Magnesium carbonate
Starch	Calcium oxide
Inulin-polysaccharide	Silicic acid
resembling starch	Magnesium silicates
Magnesium citrate	Charcoal
Sodium carbonate	Magnesium oxide
Potassium carbonate	Aluminum oxide
Calcium carbonate	Fuller's earth
Calcium sulfate	

**Solvents.**—The more common solvents are listed in Table 9-2, in the order of increasing adsorption affinity. There is such a pronounced regularity in the increasing adsorption affinity of various solvents with increased polarity, that it is possible to predict qualitatively the effect of changing the solvent. It is generally desirable to introduce the sample to the column in the most nonpolar solvent possible so that the solutes will be concentrated in a narrow zone at the top of the adsorbent bed. Then, a switch to a slightly more polar solvent will speed up the development of the chromatogram. A common practice used to change solvent polarity and eluting power is to add low percentages of alcohol or other polar solvents to a miscible nonpolar solvent such as petroleum ether or benzene. Thus one can control the polarity of the solvent to a great extent. The observed adsorption sequence of common solvents explains why alcohols, water, acids, and bases are not usually used as developing solvents for chromatography. They compete too strongly with the solute for the adsorption site, and tend to displace the solute. In effect, these solvents are good displacing solvents for removing all adsorbed solutes from the column.

TABLE 9-2. ORDER OF INCREASING SELF ADSORPTION FOR THE MORE COMMON SOLVENTS

Petroleum ether	Chloroform
Carbon tetrachloride	Dichloroethane
Cyclohexane	Alcohols
Carbon disulfide	Water
Diethyl ether	Pyridine
Benzene	Organic acids
Esters	Inorganic acids and bases

**Apparatus.**—The essential equipment is indicated in Fig. 9-4. Chemical literature is full of variations on the basic design, but modifications consist mainly in changes in the column dimensions, receiving vessel, and solvent reservoir. The ratio of column length to diameter is usually at least as great as 4:1 and often is as great as 100:1. Equipment can be set up for operations on either a micro or macro scale.

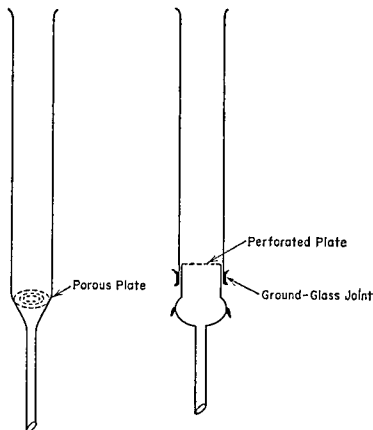


FIG. 9-4. Simple Adsorption Chromatographic Equipment.

Columns are usually packed in one of two ways. Granular adsorbents form a uniform bed when dry packed, if the sides of the column are tapped and a gentle vacuum is applied to the effluent end of the column while adsorbent is added. Beds of finely divided or powdered adsorbents are more conveniently packed by pouring a slurry of adsorbent and solvent into the column plugged with a filter pad. The liquid level must never be allowed to fall below the top of the adsorbent bed in any chromatographic operation, as air channels that prevent uniform zone development may be produced.

**Zone Detection.**—As long as colored components are chromatographed on light-colored adsorbents, zones can be visually detected without difficulty. When colorless substances are chromatographed, or when dark-colored adsorbents are used, other means of detection are required. The more common detection techniques are: (1) observance of fluorescence when solutes are exposed to ultraviolet radiation; (2) introduction to the sample of a colored component that will be adsorbed in the same region as the colorless component; (3) conversion of solutes to colored or fluorescent species by brushing or spraying the extruded column, or treating the column effluent with a color producing agent; and (4) application of physical or chemical tests to the effluent fractions or continuously. Useful properties to record are radioactivity, optical density, refractive index, pH, absorption spectra, dry weight of each fraction, conductivity, dielectric constant, and biological activity. Many of these techniques afford a means of quantitative determination as well as detection.

**Applications.**—Adsorption chromatography has been applied to the analysis of foods, condiments, drugs, dyes, inks, cosmetics, metabolism products, inorganic mixtures, amino acids, viruses, coal and petroleum products, and a host of other substances. In fact, applications are so varied that it is virtually impossible to mention all of the areas in which chromatography has been successfully applied. Because of this, only a few specific separations will be mentioned to point up the effectiveness of the method.

The separation of alpha and beta carotene,  $C_{40}H_{56}$ , is probably as striking an illustration of the resolving power of chromatography as there is. These isomers are resolved readily with a number of different adsorbent-solvent systems with the  $\alpha$ -carotene showing the least adsorption affinity. Structurally, the isomers differ only in the position of a double bond, yet, they are readily resolved.

Gasoline, kerosene and gas-oil fractions can be divided into fractions of paraffins and naphthenes, mononuclear species, and mixed aromatics in a single pass through a column. Thirty-two of the 36 possible binary mixtures made from the nine basic dyes can be resolved. Chromatography is one of the best ways of rapidly concentrating dilute solutions or purifying solvents. The ethanol content of chloroform, for example, can be reduced to less than 0.005% by a slow percolation of chloroform solution through an alumina column. Spectroscopically pure solvents, such as cyclohexane and normal hydrocarbons, are prepared by a similar technique. As much as 0.5  $\mu$ g. of nickel has been concentrated on a column of dimethylglyoxime in the presence of 5000 times as much cobalt. Numerous chromatographic schemes for inorganic analyses have been devised that are every bit as sensitive and selective as the more conventional schemes. Homogeneity tests and identification tests were outlined in the general discussion.

Chromatography offers some distinct advantages over more conventional separation techniques: the apparatus and techniques are simple and adaptable to both micro and macro sized samples; labile substances can be resolved at low temperatures in an inert atmosphere; the procedure is exceedingly selective; and both qualitative and quantitative tests can be applied to the resolved solutes. The more serious disadvantages comprise the empirical nature of the method, the low capacity of adsorbents, and the possibility of isomerization, hydrolysis, neutralization, decomposition, and precipitation of solutes on the adsorbent. Although the method is highly empirical, prediction of certain adsorption sequences on the basis of solute properties is possible. Adsorption affinities increase with molecular weight for members of a homologous series, and with the polarity of molecules, particularly organic molecules. Table 9-3 gives the order of decreasing adsorption affinity for some of the more common organic functional groups.

TABLE 9-3. ORDER OF DECREASING ADSORPTION AFFINITY OF SOME COMMON ORGANIC FUNCTIONAL GROUPS

- |   |                              |
|---|------------------------------|
| (1) Acids and bases                           | (4) Halogen compounds        |
| (2) Hydroxy, amino, thio, and nitro compounds | (5) Unsaturated hydrocarbons |
| (3) Aldehydes, ketones, and esters            | (6) Saturated hydrocarbons   |

## PARTITION CHROMATOGRAPHY

Partition chromatography is distinguished from adsorption chromatography by the use of two solvents. One is fixed on or in the adsorbent and the other is used as the developing solvent. In practice, the adsorbent, such as silica gel, is im-

pregnated with a solvent that is immiscible with the developing solvent. As the solutes are washed through the column they are partitioned between the two solvent phases. If the distribution coefficients of the solutes are different, a differential migration rate is established, which results in a separation of solutes. Partition chromatography can be treated as a pseudo-countercurrent extraction phenomenon, and solute behavior is predictable from known distribution coefficients. The  $R_f$  values and distribution coefficients,  $\alpha$ , of the solutes are related by the equation

$$R_f = \frac{A_L}{A_L + \alpha A_s}$$

where  $A_s$  = the cross sectional area of the immobile phase,  $A_L$  = the cross sectional area of the mobile phase, and

$$\alpha = \frac{\text{solute concentration in immobile phase}}{\text{solute concentration in mobile phase}}$$

Operating techniques are the same as for adsorption chromatography; only the mechanism for retarding the migration of solutes is different. The adsorbent used must not behave as an ordinary adsorbent; it must absorb or adsorb a substantial volume of the immobile phase. Table 9-4 lists some of the more common adsorbent-solvent systems used and the type of solutes resolved.

TABLE 9-4. EXAMPLES OF ADSORBENT-SOLVENT SYSTEMS USED FOR PARTITION CHROMATOGRAPHY

<i>Adsorbent</i>	<i>Immobile Phase</i>	<i>Mobile Phase</i>	<i>Solute</i>
Silica gel	Aniline	Isopropyl alcohol and benzene	Paraffins and cycloparaffins
	Water	Butanol and chloroform	Amino acids
	Methanol, water, $H_2SO_4$	Skellysolve B	Aromatic acids
Cellulose	Water	Alcohols	Amino acids
Starch	Water	Organic	Inorganic species
	Water	Butanol, benzyl, alcohol	Amino acids
Kieselguhr	Methanol and water	Ligroin-methanol	$C_7$ acids
Celite	Aqueous NaOH	Benzene	Diols
Silica	Methanolic NaOH	Iso-octane	Aliphatic acids
Powdered rubber	Butanol	Aqueous buffers saturated with butanol	Amino acids
		Chloroform, Skellysolve S, water, methanol	$C_6$ , $C_{12}$ , fatty acids



## PAPER CHROMATOGRAPHY

The term paper chromatography is reserved for the description of chromatographic procedures that employ filter paper as the migration medium. The solution to be analyzed is placed or spotted on the paper a short distance from one end and the solvent is evaporated, leaving a restricted deposit of solutes, usually less than 0.5 cm. in diameter. The end of the paper is then inserted in a solvent, and the solvent flows through the paper by capillary action. Under suitable conditions the deposited solutes are dissolved and carried from their original position by the flow of solvent. Because of the selective adsorption action of the cellulose and the elution analysis technique, it is possible to effect a complete resolution of sample components. Cellulose is electronegative in water, is highly polar, and has a great affinity for water and other polar solvents. It can act as a reducing agent and will reduce such things as permanganate, ferric salts, alkali ferricyanides, and dipicrylamines on prolonged contact. Filter paper is used in several different ways as a chromatographic medium. The paper can serve as a porous adsorbent for adsorption processes, or it can be impregnated with such things as water, rubber, high molecular weight alcohols, petroleum jelly, silicones, and various fatty derivatives. These substances, being good solvents, can serve as the immobile phase for a true liquid-liquid partitioning phenomenon. Using a developing solvent that is immiscible with the immobilized phase makes possible the distribution of solutes between the two phases. The adsorption properties of cellulose can be controlled almost at will by using it as a substrate or support for various adsorbents. Alumina, silicic acid, starch, 8-hydroxyquinoline, dimethylglyoxime, and various salts can be precipitated in the pores of the paper to give a migration medium with the flexibility of paper but the adsorbent characteristics of the precipitate.

*Apparatus.*—The basic equipment needed for the development of chromatograms on paper is usually available in all laboratories, even those with meager supplies. A reasonably airtight container, which will not absorb solvent vapors, is essential, since chromatograms or  $R_f$  values are reproducible only if the chromatogram is developed in an atmosphere saturated with the solvent and free of drafts. Glass jars, bell jars, test tubes, battery jars, graduated cylinders, hydrometer jars, specimen tanks, aquariums, clay crocks, and pipes are all usable as the chromatographic chamber if they can be provided with a tightly fitting lid. The equipment can be made quite compact by simply sandwiching the paper between two glass plates. Figure 9-5 illustrates two versatile laboratory devices for the efficient development of paper chromatograms.

Chromatograms developed in the preceding manner are referred to as one-dimensional because the solutes migrate in only one direction. A simple means of enhancing the effectiveness of paper chromatography is to develop a two-dimensional paper chromatogram. Develop the chromatogram first in one direction; remove the paper and evaporate the solvent; rotate the paper through  $90^\circ$ ; and develop the chromatogram with a second solvent flowing normal to the original solvent flow. Inasmuch as there is a great probability that adsorption affinities and  $R_f$  values for a given solute will be different in different solvents, the final position of the solutes on the chromatogram is determined by the resultant of the forces operating normal to each other. The detection of zones is essentially the same as that described in adsorption chromatography.

**Applications.**—Paper chromatography has proven very effective in resolving mixtures of amino acids, sugars, hydrolysis products, inorganic ions, and pigments. The fields of application are great; they are limited only by one's imagination and the physical limits of the technique. Because it will effectively resolve microgram quantities of materials, paper chromatography is widely used in forensic chemistry and medicine for the identification and separation of dyes, inks, cosmetics, drugs, and natural products, where only minute samples are available for analysis. Unfortunately, the procedure is ineffective in most preparative work because of the severe limitation on sample size. This disadvantage can be overcome, however,

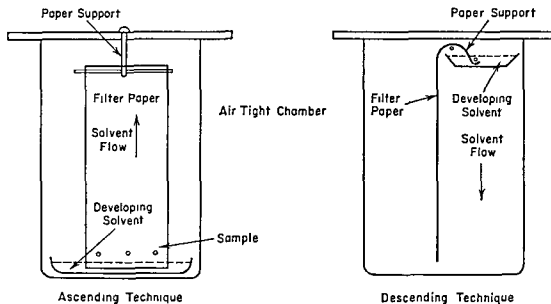


FIG. 9-5. Simple Apparatus for Paper Chromatography.

by using special papers several millimeters thick, or by using powdered cellulose as the adsorbent in columnar chromatography. The single most distinct advantage associated with paper chromatography is the fact that multiple samples can be run simultaneously on the same sheet of paper under identical conditions.

## ELECTROCHROMATOGRAPHY

If charged solutes are spotted on filter paper moistened with an electrolytic solution, and a potential gradient is established across the paper strip, the solutes will migrate through the paper to the cathode or anode according to the sign of the charge on the particle. This is electrochromatography. The flow of solvent used as the driving force in conventional paper chromatography has been replaced with a potential gradient. Differences in solute charge, adsorption affinity, and other physico-chemical factors establish characteristic migration rates for the solutes. The method is directly comparable to an elution analysis technique. A modification of this technique is a combination of solvent flow and electrostatic potential gradients operating normal to one another in the plane of the paper to produce a two-dimensional chromatogram. The final position of the solutes is then determined by the resultant of the two driving forces. Such a technique makes continuous chromatographic separations possible.

*Apparatus.*—The simplest experimental technique for electrochromatography employs a sheet of filter paper, moistened with an electrolyte, and stretched horizontally between two electrode vessels to which a potential difference is applied. The sample is spotted in the center of the strip in much the same manner that samples are applied to filter paper in paper chromatography. Solutes can now migrate in opposite directions depending on their respective charges. The paper strip is then sandwiched between glass plates (see Fig. 9-6) to prevent evaporation of solvent and to conduct excessive heat away. To achieve the same effect, the entire apparatus may be sealed in an airtight chamber saturated with solvent. Power is supplied from a d.c. source which will deliver up to 1000 v. and 100 ma.

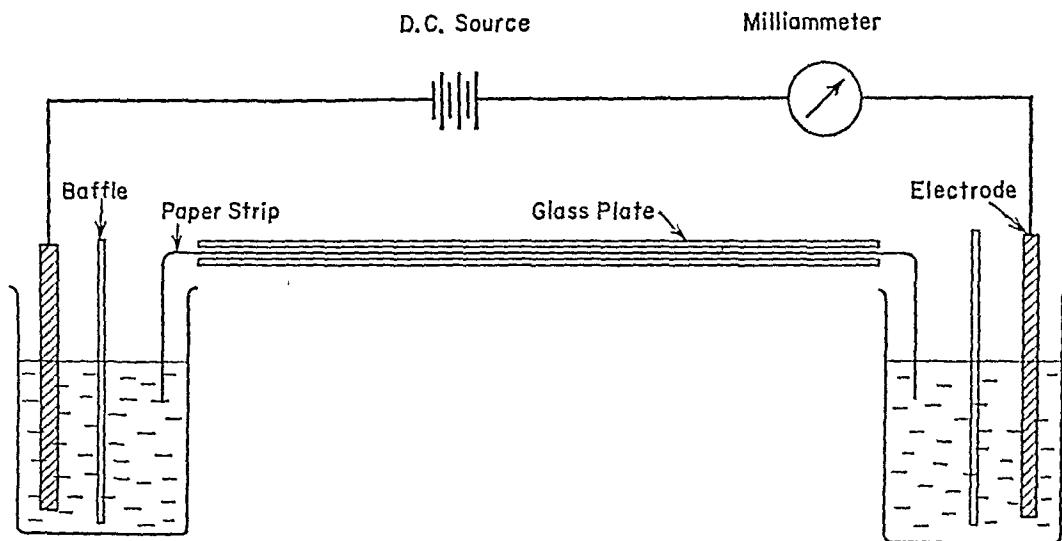


FIG. 9-6. Simple Paper Electrochromatographic Apparatus.

current. Electrodes are usually carbon or platinum to prevent sample contamination by products of corrosion.

Continuous separations are possible with more complicated apparatus. Simple equipment consists of a sheet of filter paper, moistened with an electrolyte solution, and clamped between two glass plates held in a vertical position. Electrodes contact the paper along each vertical edge. Thus, as sample solution is added continuously to the top of the paper, solutes are subjected to two forces, the flow of solvent downward, and an electrostatic potential gradient transversely. Each solute travels a characteristic path, which is the resultant of the chromatographic and electromigration factors, to the bottom of the paper. Sample components emerge separated from the lower edge of the paper, and can be collected continuously. The apparatus is illustrated in Fig. 9-7.

A discontinuous type of two-dimensional chromatography is possible with this equipment if the sample is introduced at the top in a small quantity, and washed through the paper by an elution analysis technique. Care must be taken that electrode products do not diffuse into the paper and alter the characteristics of the supporting electrolyte or developing solvent. For example, the region about the cathode may become basic and the region about the anode, acidic, during the course of the electrolysis.

The detection of solute zones on paper after an electrochromatographic devel-

opment is not significantly different from that in paper chromatography and adsorption chromatography to warrant discussion here.

**Applications.**—Electrochromatographic sequences serve for the description, comparison, and identification of substances in much the same manner that  $R_f$  values are used in paper and adsorption chromatography. The few examples of specific separations cited here are intended solely to familiarize the reader with

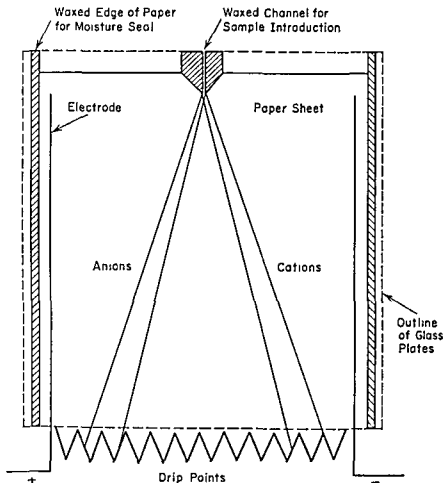


FIG. 9-7. Paper Electrochromatographic Cell Designed for Continuous Separations. (After Strain.) Note the divergence of streams of oppositely charged solutes.

the possibilities of the technique, since, obviously, it is applicable to the separation of charged particles only. Continuous separations have been reported for mixtures of: copper and silver; copper and nickel; silver, copper, nickel, and iron; aluminum and iron; yttrium and cerium; arsenic, antimony, and tin; and many others. Discontinuous separations have been effected for mixtures of: silver, mercury, and lead; iron, cobalt, nickel, and aluminum; the alkali and alkaline earth metals; and fission products.

Electrochromatography has been used for the separation of mixtures of aliphatic amines, dyes, hydrolysis products of nucleic acids, proteins, lipides, organic acids, monosaccharides, amino acids, and many other substances. Typical of what can be achieved in complex mixtures is the ready fractionation of amino acid mixtures into three groups, acidic, neutral, and basic, by the proper selection of pH

for the buffered electrolyte medium. Further separations within these groups are then possible by an adjustment of pH and the interplay of electrostatic and adsorptive forces.

## GAS CHROMATOGRAPHY

Chromatographic procedures involving a mobile gas phase can be classified into two distinct types: gas-solid chromatography (G.S.C.); and gas-liquid chromatography (G.L.C.), or gas-liquid partition chromatography (G.L.P.C.), having a liquid as the immobile phase. The liquid is immobilized by adsorption on a suitable solid such as fire brick or celite. G.L.C. enjoys a number of advantages over G.S.C. The elution bands are narrower and usually symmetrical, in contrast to the tailed bands of G.S.C., and one has a wide choice of stationary phases, making almost any separation possible. In addition, G.L.C. is amenable to theoretical treatment because the partitioning phenomenon is better understood than the adsorption process occurring in G.S.C. As a result, both practical and theoretical advancements in gas chromatography have been made almost exclusively in the field of G.L.C. It is worth noting, however, that there is very little difference in operating techniques and instrumentation for the two methods.

From its inception there has been considerable confusion in the presentation of gas chromatographic data, and much published data has been useless to other investigators. A special panel working under the auspices of the Hydrocarbon Research Group of the Institute of Petroleum of Great Britain has attempted to standardize the reporting of data. The panel's recommendations are described in an article by Ambrose, Keulemans, and Purnell.<sup>2</sup>

The recommended method of presenting data is to tabulate the values of the specific retention volumes,  $V_g$ , for various solutes or to plot  $V_g$  versus the reciprocal of the absolute temperature. These plots are usually straight lines. The retention volume,  $V_R^0$ , of a specific solute is the difference between the volume of carrier gas required to move the maximum of the solute zone through the column and the volume of the column occupied by the gaseous phase, the volume measurements being made between the points of sample injection and detector. The retention volume,  $V_R^0$ , is converted to a standard value,  $V_g$ , by calculating the value of the retention volume at standard temperature and pressure per unit weight of the solvent. In routine analyses, though, a suitable standard is added to the sample mixture and retention volumes are measured in relation to the standard. Thus any changes occurring in operating conditions affect standard and solutes alike, and relative retention volumes are not changed. This leads to the most popular method of reporting data, which is to plot the log of the relative retention volumes versus  $1/T$ . In such cases the data should be given for at least two temperatures along with the partition coefficient and  $V_g$  for the reference or standard solute.

**Instrumentation.**—Space will not permit a detailed discussion here of instrumentation used in gas chromatography but the essential components will be mentioned. Figure 9-8 is a block diagram of a typical gas chromatographic unit. The carrier gas is usually helium but hydrogen, nitrogen, oxygen, carbon dioxide, and air are also used. The column is either a glass or metal tube (4 to 8 mm. I.D.), packed with solid adsorbent, and coated with the appropriate nonvolatile solvent.

<sup>2</sup> Ambrose, D., Keulemans, A. and M., and Purnell, J. H., *Anal. Chem.*, **30**, 1582, 1958.

Crushed fire brick (30/50 or 30/60 mesh size) or chromosorb (a diatomaceous earth) are the most common adsorbents. Table 9-5 lists the more common solvents or substrates used to coat the adsorbent. In most instruments the column and detector are thermostated at temperatures up to 200°C. Liquid samples are generally injected with a hypodermic syringe in volumes of 0.1 to 10  $\mu$ l., whereas gaseous samples are swept from a gas pipet with the carrier gas. Detectors based on changes in the thermal conductivity, dielectric constant, ionizability, radioactivity, and heat of combustion of the effluent gas stream are widely used for the

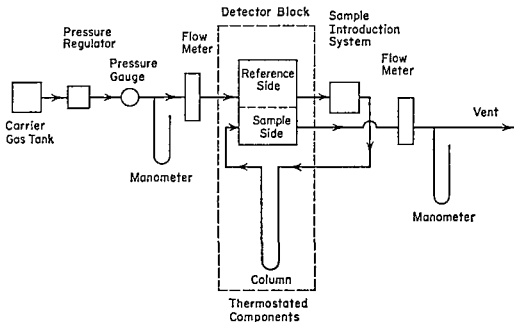


FIG. 9-8. Block Diagram of a Typical Gas Chromatography Unit.

detection of resolved solutes. Of these, thermal conductivity types are used almost exclusively in commercial instruments.

A recent significant advance in instrumentation was the introduction of capillary columns that do not use a packing. The columns are approximately 0.01 inch I.D. and 100 to 300 feet long. The walls of the capillary are coated with the nonvolatile solvent. A maximum sample charge of 1 to 2 mg. is permissible. The columns can be formed into compact coils, are easily prepared and thermostated, and have unusually high separation efficiencies. Analyses are also more rapid than with packed columns.

**Applications.**—Under a definite set of experimental conditions, the retention volume is a characteristic property of a solute, and can be used in its identification in a fashion analogous to the use of  $R_f$  values in adsorption or paper chromatography. A more sophisticated qualitative test for unknowns involves a plot of the log of the retention volume of members of a homologous series versus the number of carbon atoms. Such plots yield straight lines which are clearly useful for the identification of unknown compounds in a given class. The resolving power of the technique can be exemplified with the following examples. Petroleum fractions containing 20 or more constituents in any boiling fraction can be resolved. In the coal tar fraction, boiling up to 218°C., for example, 52 compounds have been separated and identified. Of these, 27 compounds were separated and

TABLE 9-5. SUBSTRATE MATERIALS USED IN GAS-LIQUID CHROMATOGRAPHY AND THE TYPES OF SUBSTANCES REPORTED SEPARATED ON EACH

<i>Substrate Material</i>	<i>Separation</i>
<i>n</i> -Dodecane	C <sub>6</sub> hydrocarbons
<i>n</i> -Octadecane	C <sub>7</sub> to C <sub>9</sub> hydrocarbons
<i>n</i> -Decane	Low boiling hydrocarbons
2,5-Hexanedione	C <sub>4</sub> hydrocarbons and low boiling hydrocarbons
Acetonylacetone	C <sub>3</sub> to C <sub>5</sub> hydrocarbons and low boiling hydrocarbons, including olefins and diolefins
Dibutylphthalate	General hydrocarbons
Squalane	Hydrocarbons
Di-2-ethylhexyl sebacate	General hydrocarbons, chlorinated hydrocarbons
Aircraft engine oil (Bright Stock)	High boiling hydrocarbons and general separation of high boilers
Silicone 550	General hydrocarbons and organometallics
Dimethylformamide	Olefins and acetylenes
Dimethyl sulfolane (Oxydipropionitrile)	Olefins from paraffins, olefins, pentenes, and hexenes
Tri-isobutylene	C <sub>2</sub> and C <sub>3</sub> compounds, including paraffins, olefins, and acetylenes
Diethylene glycol mono-ethyl ether	C <sub>3</sub> to C <sub>5</sub> compounds, including olefins and diolefins
Silicone 550 and stearic acid	Fatty acids
Apiezon L	High boiler, general purpose, esters of fatty acids
Paraffin wax	Amines
Carbowax 4000	Amines and water
Dioctyl phthalate	
Dinonyl phthalate	General purpose including ketones and esters, fluorinated hydrocarbons
Tricresyl phosphate	
Silicone 702	
Narcoil 40	
Polypropylene glycol	Separation of polar and nonpolar compounds
High vacuum silicone grease	High boiling compounds
1-Chloronaphthlene	Isomeric xylenes
Silver nitrate in polyethylene glycol	Low boiling olefins
Hydrogenated vegetable oil	N-acetyl butyl esters of amino acids

identified for the first time by gas chromatography. The technique has been used quite successfully to resolve isomers, aldol condensation products, derivatives of amino acids, long chain fatty acids, numerous petroleum products, automobile exhaust products, air pollutants, volatile food products, metal chlorides, metal acetylacetonates, and to identify and determine the extent of alcoholic intoxication from the breath.

Gas chromatography is extremely selective, rapid, and easily adapted to automatic recording and control operations. Columns can be used repeatedly without repacking, and sample components are diluted only slightly by the carrier gas. Separations are restricted to readily volatile substances, which are stable at the column temperature, and only small quantities of sample can be used, which precludes the use of the technique in general preparative work.

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## Chapter 10

# ION EXCHANGE METHODS IN ANALYSIS

By Harold F. Walton

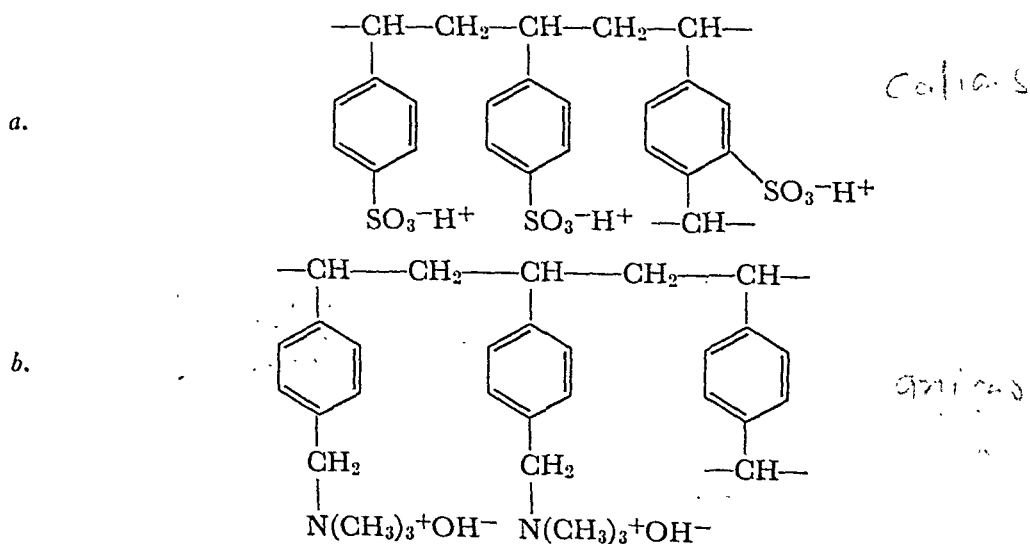
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In ion exchange, ions of one kind in a solution are replaced by ions of another kind, but of similar charge, by contact with an insoluble material called an *ion exchanger*. As a glance at any current journal will show, ion exchange has become one of the routine tools of the analytical chemist.

### ION EXCHANGING MATERIALS

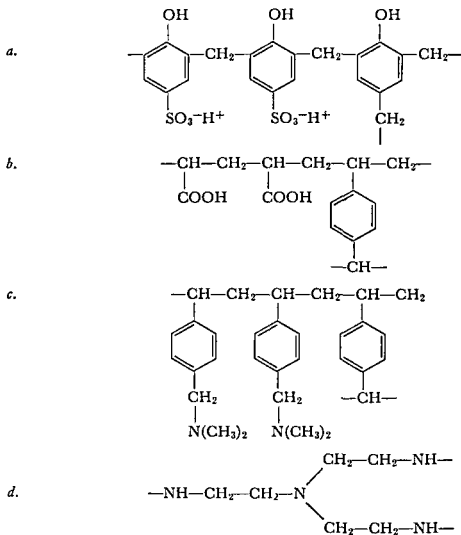
**Structure.**—The ion exchangers used in analytical work are crosslinked polyelectrolytes. Usually they are resinous in nature. To many people the term “ion exchange resin” and “ion exchanger” are synonymous. However, inorganic ion exchangers have their uses too, and a new class of synthetic inorganic exchangers has come into being in recent years.

Ion exchangers contain ionic functional groups attached to a polymer network. The range of possible ionic groups and polymers is very wide, and a great variety of materials has been synthesized. For routine analytical use, however, only a few of these need be considered. First in importance are the resins based on crosslinked polystyrene:



By copolymerizing styrene and divinyl benzene and sulfonating the product, a *cation exchanger* is obtained; by chlormethylating the copolymer and then treating with a tertiary amine, *anion exchangers* are formed. These two types of exchanger suffice for most analytical purposes. They are highly ionized in their hydrogen and hydroxyl forms, respectively, as well as in their salt forms.

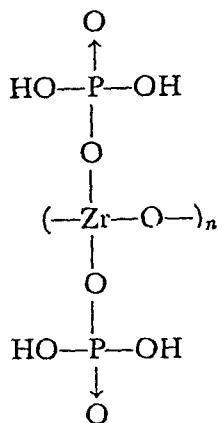
For certain applications in organic and biochemical analysis (and in preparative work) weakly acidic or weakly basic ion exchangers are desired. Typical chemical structures that give these properties are shown below:



It is obviously possible to have strongly and weakly acidic (or basic) groups in the same resin. A special case of a bifunctional cation exchange resin is the sulfonated phenolic type (see diagram). Among the many functional groups that can be introduced into ion exchange resins are the phosphoric acid group, the sulfhydryl group, and the iminodiacetate group,  $-N(CH_2COOH)_2$ . Resins of this last type are amphiprotic and have chelating properties. The analytical applications of such resins seem to be limited, but have been little explored.

The new class of inorganic exchangers, mentioned above, is based on the hydrous oxides of the fourth, fifth and sixth groups of the periodic system, principally,  $ZrO_2$ ,  $SnO_2$ ,  $V_2O_5$ ,  $P_2O_5$ ,  $MoO_3$  and  $WO_3$ . Hydrous zirconium oxide, for

example, exhibits amphotropic properties. It acts as a weakly basic anion exchanger below pH 6, and as a weakly acidic cation exchanger above this pH. Zirconium phosphate is naturally more acidic in nature and behaves as a cation exchanger over the whole pH range. A hypothetical structure for this material is:



When fully ionized (above pH 12) this material should have an equivalent weight of 75, or an ion exchange capacity of 13 meq. per g., in contrast to sulfonated polystyrene resin with a capacity of 5 meq. per g.

These exchangers are stable to heat and radiation and are very effective in separating ions of the alkali and alkaline earth metal groups.<sup>1,2</sup>

**Physical and Chemical Properties of Ion Exchange Resins.**—Resins based on polystyrene are supplied in the form of beads that are almost perfect spheres. They are available in any desired mesh size from about 18 mesh (1 mm. diameter, measured when wet) down to colloidal size. The size ranges 50 to 100 mesh and 100 to 200 mesh are best for most analytical work.

Dry resin beads swell considerably when placed in water. The extent of swelling is controlled by the *crosslinking*. The degree of crosslinking of styrene-divinylbenzene copolymers is expressed as the percentage of divinylbenzene used in making the polymer. For most practical purposes, 8% crosslinking is best. The higher the crosslinking, the more ions are held per unit volume of swollen resin, and the greater is the selectivity. On the other hand, the exchange reactions are slower, and the larger ions penetrate extremely slowly or not at all. Resins with low crosslinking (4% and less) react faster with large ions but have the disadvantage that their volume may change significantly when one eluting solution is substituted for another. In exacting chromatographic separations, such as the separation of amino acids, this may offset the advantage of greater permeability.<sup>3,4,5</sup>

<sup>1</sup> Kraus, K. A., Phillips, H. O., Carlson, T. A., and Johnson, J. S., Proc. Second United Nations Conference on Peaceful Uses of Atomic Energy, Vol. 28, p. 3, 1958.

<sup>2</sup> Amphlett, C. B., *ibid.*, p. 17.

<sup>3</sup> Stein, W. H., and Moore, S., Cold Spring Harbor Symposia Quant. Biol., 14, 179, 1949; Moore, S., and Stein, W. H., J. Biol. Chem., 192, 663, 1951; Moore, S., and Stein, W. H., *ibid.*, 211, 893, 907, 1954.

<sup>4</sup> See also chapter by P. B. Hamilton, in Calmon, C., and Kressman, T. R. E., (Eds.), Ion Exchangers in Organic and Biochemistry, Interscience Publishers, Inc., New York 1957.

<sup>5</sup> Hamilton, P. B., and Anderson, R. A., Anal. Chem., 31, 1504, 1959.

Polystyrene-type ion exchange resins have good chemical stability. Sulfonated polystyrene cation exchangers are attacked slowly by strong oxidizing agents at temperatures above 80°C.;<sup>6</sup> at 100°, with hydrogen ions as the replaceable cations, these resins lose sulfuric acid very slowly, but if the hydrogen ions are replaced by sodium ions, the resins are stable up to 200°C. in presence of water.<sup>7</sup> In other words, these resins are completely resistant to chemical attack under normal operating conditions. Anion exchange resins in the salt form are stable up to 100° and above, but the hydroxyl forms break down appreciably at temperatures above 50° to 60°.

The bead type resins are amber colored or almost white. Sulfonated polystyrene resins used to be dark brown colored owing to degradation during the sulfonation process. They are now available in the "white" grade, actually light yellow in color, which is an advantage where colored ions are being exchanged and is also a sign of better chemical characteristics.

Table 10-1 lists a few of the resins commercially available. Methods for determining such characteristics as moisture content, exchange capacity, degree of swelling, and acid or basic strength are described in manuals and reference works.<sup>8, 9, 10</sup>

## ION EXCHANGE COLUMNS

Ion exchangers are almost always used in columns. By flowing a solution through a column, the ion exchange reaction, which is intrinsically reversible, can be made to go to completion, within the limits of analytical detection, in any desired direction.

**Description of Column.**—A useful form of column is shown in Fig. 10-1. This column will hold 10 to 15 ml. of resin (bulk volume); 1 ml. of column volume holds about 2 milliequivalents of sulfonated polystyrene cation exchanger or 1 milliequivalent of strong base polystyrene type anion exchanger assuming 8% crosslinking in each case. The resin is supported on a coarse sintered glass plate. A plug of glass wool can also be used. The bulb at the top of the column is not essential, but it is convenient for holding solution and also for backwashing the resin if this should be necessary.

The size of the column depends on the work in hand. Resin columns can be scaled up or down over a very wide size range, and it is a common error to use a larger column than necessary. This requires inconveniently large volumes of solutions and therefore wastes time. With very small columns one must, of course, use fine mesh resins.

**Packing the Column.**—The resin in the column must be packed as uniformly as possible to avoid "channelling" and ensure flat elution bands. Dry resin should never be placed in the column. It must first be stirred with water in a beaker and allowed to remain there for 15 minutes or whatever time is necessary for the

<sup>6</sup> Saldadze, K. M., and Demonerik, Z. G., *Research in Ion Exchange Chromatography*, p. 96. Translated by Consultants Bureau, Inc., New York, 1958.

<sup>7</sup> Kraus, K. A., and Raridon, R. J., *J. Phys. Chem.*, **63**, 1901, 1959.

<sup>8</sup> Kunin, R., *Ion Exchange Resins*, 2nd ed., John Wiley and Sons, Inc., New York, 1958.

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<sup>10</sup> Salmon, J. E., and Hale, D. K., *Ion Exchange: A Laboratory Manual*, Academic Press, New York, 1959.

TABLE 10-1. COMMERCIALY AVAILABLE ION EXCHANGE RESINS

Ex-changer Type	Chemical Nature	Form	Functional Group	Commercial Designations <sup>a</sup>
Cation	Sulfonated polystyrene, strong acid	Beads	SO <sub>3</sub> H	Amberlite IR-120, Dowex-50, Duolite C-20, Permutit Q, Zerolit 225
Cation	Sulfonated phenolic, strong acid	Gel	SO <sub>3</sub> H Phenolic OH	Duolite C-3, Zerolit 215
Cation	Polyacrylic acid, weak acid	Beads	COOH	Amberlite IRC-50, Duolite CS-101, Zerolit 226
Anion	Quaternary ammonium, type 1, strong base	Beads	CH <sub>2</sub> NR <sub>3</sub> OH	Amberlite IRA-400, Dowex-1, Duolite A-42, De-Acidite, Zerolit FF
Anion	Quaternary ammonium, type 2, strong base	Beads	CH <sub>2</sub> NR <sub>2</sub> OH   CH <sub>2</sub> CH <sub>2</sub>   OH	Amberlite IRA-410, Dowex-2, Duolite A-40
Anion	Primary, secondary and tertiary amine, weak base	Gel & beads	CH <sub>2</sub> NH <sub>2</sub> , etc.	Amberlite IR-4B, IR-45; Dowex-3; Duolite A-7, A-14; Zerolit G
Chelating	Iminodiacetic acid	Beads	CH <sub>2</sub> N (CH <sub>2</sub> COH) <sub>2</sub>	Dowex A-1

<sup>a</sup> *Manufacturers:* Dowex, Dow Chemical Co., Midland, Michigan; Amberlite, Rohm and Haas Co., Philadelphia; Duolite, Chemical Process Co., Redwood City, California; Permutit and De-Acidite, Pfaudler-Permutit Co., New York; Zerolit, United Water Softeners Ltd., London.

swelling to be completed. One may remove the "fines" by stirring the resin in water, letting it settle for a minute or two, decanting, then adding more water and repeating the process. Then the resin is stirred with water and immediately poured into the column. With mesh sizes of 100 and finer, the rate of settling is sufficiently slow for the larger particles to settle at the bottom of the column and the smaller at the top without further treatment. For the coarser particle sizes it is desirable, after pouring the resin into the column, to "backwash," i.e., to pass water up through the bottom of the column to float the resin in the upper bulb. Then the water flow is stopped and the resin allowed to settle. Naturally the column must be as nearly vertical as possible (a visual estimate is sufficient).

bound more strongly by the exchanger than *B*. When this front reaches the end of the column, the concentration of *A* in the effluent solution rises very quickly from near zero to the value in the influent solution. If, on the other hand, ion *B* is more strongly bound by the exchanger than *A*, the front will become more diffuse as it moves down the column.

The analyst can improve the sharpness of the fronts by raising the concentration of ion *A*. This will be particularly effective if *A* has a smaller charge than *B*, so that two or more ions of *A* displace one of *B*.

*b.* In elution chromatography the ions, *B*, being displaced from the column constitute only a very small proportion of the ions in the column; *A* is less strongly bound than *B*, and the ratio of *B* to *A* is everywhere small, so that the distribution ratio,  $D = (\text{quantity of } B \text{ in resin}) \div (\text{quantity of } B \text{ in solution})$  in a given small segment of the column, can be considered a constant. If this is so, then the volume of solution that must flow past the band of ions *B* to move it from one end of the column to the other is

$$\bar{V} = DV_c$$

where  $V_c$  = the *column volume* = the volume of solution retained between the resin particles in the column. This simple relation<sup>16</sup> helps to predict the separation of ions by elution chromatography.

*c.* The more nearly equilibrium is reached in the column, the sharper are the elution bands and displacement fronts. The speed of ion exchange depends on the rate at which ions can diffuse within the resin,<sup>17</sup> and is governed primarily by the rate at which the ions that are inside the resin granules can move out.<sup>18</sup> In other words, large ions go into the resin faster than they come out. Elution bands can be sharpened by using finer resin particles, higher temperatures, and slower flow rates.

## REPRESENTATIVE ANALYTICAL APPLICATIONS

*Determination of Total Electrolyte in a Solution.*—This is probably the simplest application of ion exchange to chemical analysis. The solution to be analyzed is passed through a column of sulfuric acid cation exchange resin in the hydrogen form, which is then rinsed with two or three column volumes of water. The cations in the solution are replaced by an equivalent amount of hydrogen ions; the effluent solution and the rinse are titrated with standard base.

The commonest use of this technique is to measure the total salt content of natural water. Here the displacing cations are mainly calcium and sodium; the sodium ions are not strongly absorbed by the resin, and the hydrogen ions of the resin should be in at least threefold excess over the cations in the solution. Good results are obtained with a 10-ml. column of 50- to 100-mesh sulfonated polystyrene resin, 8% crosslinked, and 25- to 50-ml. samples of waters containing about 10 mg. per l. total salts. Two or three such samples may be passed before the column needs to be regenerated (which is done by passing hydrochloric acid and then rinsing). Two titration procedures may be used:

<sup>16</sup> Mayer, S. W., and Tompkins, E. R., J. Am. Chem. Soc., **69**, 2866, 1947.

<sup>17</sup> Boyd, G. E., and Soldano, B. A., J. Am. Chem. Soc., **75**, 6091, 1954.

<sup>18</sup> Helfferich, F., and Plesset, M. S., J. Chem. Physics, **28**, 418, 1958.

change resin containing exchangeable hydrogen ions. Ferric ions are held back, and the solution emerging from the column contains all the sulfate with no cations but hydrogen ions. Sulfate can be determined in this effluent without interference.

A well-known procedure based upon this principle is the determination of sulfur in pyrites.<sup>33</sup> The rock is dissolved in a mixture of hydrochloric acid, nitric acid, and bromine; this oxidizes sulfur to sulfuric acid. Bromine and nitric acid are then removed by evaporation, and the solution containing ferric ions, sulfate ions, and chloride ions is passed through a cation exchange resin column. Since hydrogen ions are also present, the resin must be in stoichiometric excess over the ferric and other metal cations, but the excess need not be a large one. The bed is rinsed with 2 to 3 column volumes of water. The combined effluent and rinse can either be analyzed gravimetrically or be made to known volume, aliquots can be titrated with standard base and silver nitrate, and the sulfate determined by the difference between the total acidity and the chloride.

Similar procedures have been described for determining phosphate in phosphate rock<sup>34</sup> and arsenate in insecticide powders.<sup>35</sup> Caution is needed, however, since some of the phosphate may be retained as a positively charged ferric phosphate complex ion on the cation exchanger.

Sulfate can be titrated with barium chloride (or, better, perchlorate) in 40% alcohol using an adsorption indicator such as Alizarin Red S or "Thorin."<sup>36</sup> Most cations interfere by coprecipitation, and the solution to be analyzed is therefore first passed through a cation exchange resin in the hydrogen form. A variant on this method uses lead nitrate as titrant and dithizone as indicator, again with preliminary ion exchange treatment.<sup>37</sup>

Many similar examples could be cited, but a noteworthy example of the preliminary removal of interfering cations before determining anions is in the photometric determination of  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{F}^-$ , and  $\text{Cl}^-$  by their reaction with sparingly soluble salts of chloranilic acid.<sup>38</sup>

**Separations Through Complex Ions.**—An effective way to separate metals is to combine ion exchange with complex ion formation. If conditions exist where one metal forms a cation in solution while another forms an anion, and the various equilibria are favorable, these metals can be separated by ion exchange.

**Anion Exchange in Hydrochloric Acid.**—The best way to do this is by anion exchange in hydrochloric acid solutions. Most metals form anionic chloride complexes, and between different metals there are wide differences in the stabilities of these complexes and their ease of attachment to anion exchange resins. The most stable complexes are absorbed by anion exchangers from dilute hydrochloric acid; the least stable complexes are absorbed from concentrated hydrochloric acid or not at all. By absorbing a group of metal ions from concentrated acid and eluting with successively more dilute acid it is possible to separate many metals.<sup>39, 40</sup>

<sup>33</sup> Whiteker, R. A., and Swift, E. H., *Anal. Chem.*, **26**, 1602, 1954.

<sup>34</sup> Helrich, K., and Rieman, W., III, *Ind. Eng. Chem., Anal. Ed.*, **19**, 651, 1947.

<sup>35</sup> Odencrantz, J. T., and Rieman, W., III, *Anal. Chem.*, **22**, 1066, 1950.

<sup>36</sup> Fritz, J. S., and Freeland, M. Q., *Anal. Chem.*, **26**, 1593, 1954.

<sup>37</sup> White, D. C., *Mikrochim. Acta*, 1960, 282.

<sup>38</sup> Bertolacini, R. J., and Barney, J. E., *Anal. Chem.*, **29**, 281, 1187, 1957; *ibid.*, **30**, 202, 1958.

<sup>39</sup> Kraus, K. A., and Nelson, F., *Proc. First United Nations Conference on Peaceful Uses of Atomic Energy*, Vol. 7, p. 113, 1955; Chap. 23 in Hamer, W. J. (Ed.), *The Structure of Electrolytic Solutions*, John Wiley and Sons, Inc., New York, 1959.

<sup>40</sup> Jeuttsch, D., *Z. anal. Chem.*, **152**, 134, 1956; **150**, 241, 1956 and earlier papers.

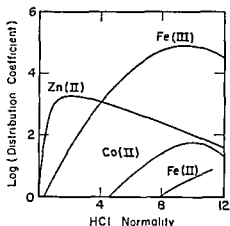
To illustrate the technique, cobalt, nickel, and iron(III) can be separated as follows. Prepare a solution containing 1 millimole each of  $\text{FeCl}_3$ ,  $\text{CoCl}_2$  and  $\text{NiCl}_2$  in 20 ml. 9 N HCl, and a resin column as illustrated in Fig. 10-3, containing 10 to 12 ml. of type 1 quaternary amine resin, 100 to 200 mesh. It is very important that the resin be washed free of soluble organic impurities. Wash the column with 9 N HCl; then pour the solution to be analyzed on top of the column and let it flow in slowly. Nickel is not absorbed and soon appears in the effluent.

Rinse with about 20 ml. 9 N HCl to recover all the nickel, then change the receiver.

Now pass 4 N HCl. This displaces the cobalt. The color of the effluent will show when this has been washed out. To displace the iron, pass 0.1 N HCl. The metals in the effluents can be determined in various ways, titration with EDTA being one of the best.

Kraus and Nelson<sup>39</sup> have expressed their data in the form of graphs of distribution coefficients against hydrochloric acid concentration for many elements. Examples of such curves are given in Fig. 10-2. It will be noted that there is an optimum chloride concentration for maximum absorption. Raising the chloride concentration stabilizes the complex ions at first but then competes with these ions for the exchange sites of the resin.

FIG. 10-2. Adsorption of Metals as Chloride Complexes by Type 1 Strong Base Anion Exchanger.



The data may briefly be summarized as follows:

*Metals not absorbed* ( $D < 10$ ): alkali and alkaline earth metals; Al, Y, rare earths, Ac; Th; Ni.

*Metals weakly absorbed* ( $D < 10$ ): Sc, Ti(III), V(IV), Cr(III), Mn, Tl(I).

*Metals moderately absorbed* ( $D < 100$ ): Ti(IV), Fe(II), Co, Cu(II), Ge, As, Se, Mo, Rh(III), In, W(VI), Ir(III), Pb.

*Metals strongly absorbed* ( $D > 100$ ): V(V), Cr(VI), Fe(III), Cu(I), Zn, Ga, Zr, Ru, Rh(IV), Pd, Ag, Cd, Sn(IV), Sb, Te(IV), Re, Os, Ir(IV), Pt(IV), Au, Hg, Tl(III), Bi, Po, U(VI).

With the help of such data many useful separations have been worked out. For example, Ni, Cu, Zn and Cd in silver solder are separated by hydrochloric acid elution and titrated with EDTA;<sup>41</sup> small quantities of thorium are separated from uranium and much bismuth in analyzing nuclear fuels;<sup>42</sup> and a scheme for silicate rock analysis has been devised using anion and cation exchange resins.<sup>43</sup> The separations are clean and rapid, and are useful in separating small amounts of short-lived radioactive elements from cyclotron targets.

**Anion Exchange in Presence of Other Ligands.**—Anionic complexes of metals formed with other ligands can obviously be used for separations by anion exchange. Fluoride complexes can be used, and anion exchange separations in mixed HCl-HF solutions have been explored;<sup>44</sup> these have advantages for elements

<sup>41</sup> Jones, S. L., *Anal. Chim. Acta*, **21**, 532, 1959.

<sup>42</sup> Milner, G. W. C., and Nunn, J. H., *Anal. Chim. Acta*, **17**, 494, 1957.

<sup>43</sup> Yoshimura, J., and Waki, H., *Japan Analyst*, **6**, 362, 1957; *Anal. Abstracts*, **5**, 1871, 1958.

<sup>44</sup> Nelson, F., Rush, R. M., and Kraus, K. A., *J. Am. Chem. Soc.*, **82**, 339, 1960.



of groups 4 and 5. The sulfate complex of uranium(VI) may be absorbed selectively by anion exchangers for analysis<sup>39,45</sup> just as it is in the refining of uranium ores, and the acetate complex has been used to concentrate traces of U(VI) for geochemical analysis.<sup>46</sup> Many similar applications could be cited.

**Cation Exchange.**—It is just as logical, *a priori*, to use cation exchangers for separations based on differential complex formation as to use anion exchangers. Yet cation exchange is not as selective, and the separations are not as clean nor as versatile as those by anion exchange. An example of cation separation based on differential stability of chloride complexes is the successive elution of Fe(III), Zr and Th from a cation exchange resin column by 1 M HCl, 4 M HCl and EDTA, respectively.<sup>47,48</sup> Citrate solutions have been used to elute metals selectively,<sup>49</sup> and so have EDTA solutions of graded pH.<sup>50</sup> Both citrate and EDTA eluants have the disadvantage that, before the metal that has been removed from the column can be analytically determined, the excess of organic compound must be destroyed. Hydrochloric acid solutions, on the other hand, can simply be evaporated if the excess of acid interferes in the analysis.

**Elution Chromatography.**—Two ionic species having charges of the same sign can be separated by ion exchange if one is more strongly bound by the exchanger than the other. Two factors enter here: the selectivity of the exchanger itself and the various ionic equilibria in the solution. The separations discussed in the last section were examples of elution chromatography; complexing agents are often used as eluants.

[In the elution technique a small amount of the mixture to be separated is absorbed at the top of an ion exchange column. An eluting solution is then passed which displaces the ions down the column at differing speeds. Each species moves down the column as a gradually broadening band, and, if the column is long enough, the bands become separated so that each species emerges in practically pure form, except, of course, for the accompanying eluant. To obtain separate bands it is necessary for the eluting ions to be less strongly bound than the ions being displaced; i.e.,  $D \gg 1$  (see p. 235).]

The solution leaving the column is generally collected in many successive small fractions by means of an automatic fraction collector (Fig. 10-3). Each is then analyzed, and the concentrations of the eluted species are plotted against the volume to give graphs such as the one shown in Fig. 10-4. In the ideal case of a perfectly packed column, infinitesimal amounts of eluted ions and complete attainment of equilibrium within each "theoretical plate," the graphs would be symmetrical and follow the Gauss error function. In actual practice they are liable to be lopsided and show "tailing," especially if the amount of material is not small compared to the capacity of the column. "Tailing" can be reduced by increasing the displacing power of the eluant—for example, by raising its concentration or changing its pH, after the peak of the band is passed. In "gradient elution" the eluant composition is changed continuously as the run proceeds, giving better spacing of the bands and narrower and more uniform bands. The gradient technique has been

<sup>45</sup> Fisher, S., and Kunin, R., *Anal. Chem.*, **29**, 400, 1957.

<sup>46</sup> Hecht, F., Korkisch, J., Patzak, R., and Thiard, A., *Mikrochim. Acta*, 1956, p. 1283.

<sup>47</sup> Strelow, F. W. E., *Anal. Chem.*, **31**, 1201, 1959; *ibid.*, **32**, 363, 1185, 1960.

<sup>48</sup> Samedy, S. R., Thesis, University of Colorado, 1958.

<sup>49</sup> Brown, W. E., and Rieman, W., III, *J. Am. Chem. Soc.*, **74**, 1278, 1952.

<sup>50</sup> Fritz, J. S., and Umbreit, G. R., *Anal. Chim. Acta*, **19**, 509, 1958.

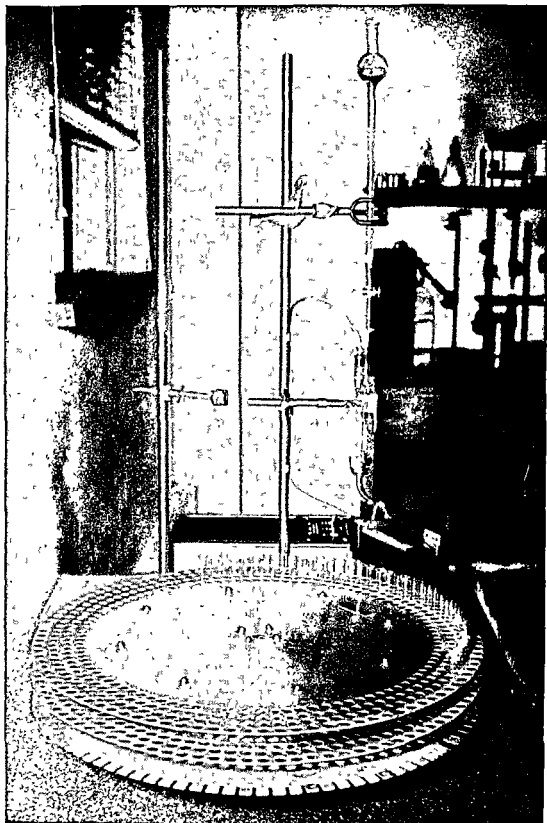


FIG. 10-3. Automatic Fraction Collector for Chromatography.

applied to separation of the amino acids<sup>51,52</sup> and the rare earth elements.<sup>53,54</sup> The separation of the rare earths by ion exchange elution is one of the major triumphs of inorganic chemistry in recent years.<sup>55</sup> Citrate, lactate, or EDTA solutions are used for elution, and the process is really one of differential complex formation inasmuch as the resin has little selectivity in itself. Other examples of ion exchange elution chromatography in inorganic chemistry are the separation of the alkali and alkaline earth metals and the halide ions.<sup>56</sup> These do not involve complex ion formation. For the separation of potassium, rubidium, and cesium or of calcium, strontium, barium, and radium from one another, ion exchange is by far the most useful method, and the most selective exchangers are inorganic ones; zirconium phosphate exchanger, with ammonium chloride as the eluant, is excellent for separating the alkali metals, whereas zirconium molybdate

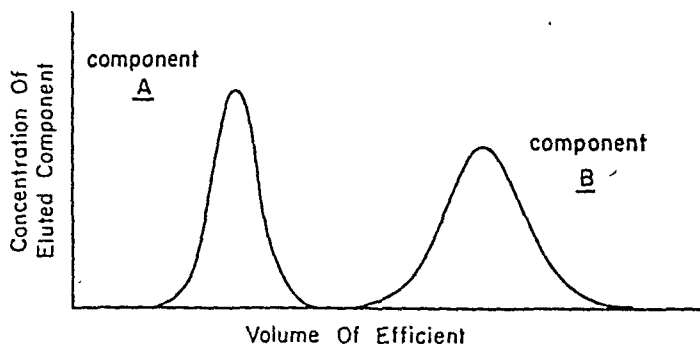


FIG. 10-1. Idealized Elution Curve for Separation of Two Components.

is excellent for separating the alkaline earth ions.<sup>57</sup> The method is applicable to short-lived radioactive isotopes.<sup>58</sup>

Because the binding to an exchanger is stronger, the higher the charge on the ions, it is easy to separate the alkali metals as a group from the alkaline earth metals.<sup>57</sup> In silicate rock analysis the metals sodium and potassium are easily separated from other constituents and from each other.<sup>59</sup> Separations of groups of cations based on their charge have been proposed,<sup>60</sup> and special applications suggest themselves, such as the separation of orthophosphate, pyrophosphate, and condensed phosphate ions by anion exchange.<sup>61</sup>

The major analytical use of ion exchange elution chromatography is in the biochemical field. Amino acid mixtures are routinely analyzed by elution from cation exchange resin columns, and standardized, automatic equipment for the pur-

<sup>51</sup> Alm, R., Williams, R. J. P., and Tirelius, A., *Acta Chem. Scand.*, **6**, 826, 1952.

<sup>52</sup> Williams, R. J. P., *Analyst*, **77**, 905, 1952.

<sup>53</sup> Freiling, E. C., *J. Am. Chem. Soc.*, **77**, 2067, 1955.

<sup>54</sup> Nervik, W., *J. Phys. Chem.*, **59**, 690, 1955.

<sup>55</sup> Schubert, J., Chap. 8 in F. C. Nachod (Ed.), *Ion Exchange*, Academic Press, New York, 1949.

<sup>56</sup> De Geiso, R. C., Rieman, W., III, and Lindenbaum, S., *Anal. Chem.*, **26**, 1840, 1954.

<sup>57</sup> Kraus, K. A., Phillips, H. O., Carlson, T. A., and Johnson, J. S., *Proc. Second United Nations Conference on Peaceful Uses of Atomic Energy*, Vol. 28, p. 3, 1958; Amphlett, C. B., *ibid.*, p. 17.

<sup>58</sup> Crouch, E. A. C., Corbett, J. A., and Willis, H. H., *AERE Report C/R 2325*, 1957; *Anal. Abstracts*, **5**, 2109, 1958.

<sup>59</sup> Reichen, L. E., *Anal. Chem.*, **30**, 1948, 1958.

<sup>60</sup> Fritz, J. S., and Karraker, S. K., *Anal. Chem.*, **31**, 921, 1959.

<sup>61</sup> Lindenbaum, S., Peters, T. V., and Rieman, W., III, *Anal. Chim. Acta*, **11**, 530, 1954.

pose is now available. The techniques have been developed by Moore and Stein<sup>62</sup> and Hamilton and Anderson.<sup>63</sup> Columns about 100 cm. long, containing some 150 milliequivalents of resin, will separate some 75 micromoles of a mixture of 25 amino acids, and up to 50 components can be separated if necessary. The columns are water-jacketed for temperature control; the temperature is about 50°C. and is raised in stages during the elution. The resin is a sulfonated polystyrene of particle diameter about 40 microns, and the more uniform the particles, the sharper are the bands and the faster the permissible flow rate.<sup>64</sup> The eluant is a citrate buffer whose pH is raised in steps during the elution from about 3.0 to 5.0.

Peptides,<sup>65</sup> nucleic acid derivatives,<sup>66</sup> fruit acids<sup>67</sup> and even carbohydrates<sup>68</sup> can be separated by ion exchange chromatography. Carbohydrates may be separated by forming their negatively charged borate complexes and separating these on an anion exchanger. Even uncharged species, however, can be separated on columns of ion exchange resins, since attractive forces operate in addition to the purely electrostatic forces.<sup>69</sup> Some of the separations of organic compounds that have been performed by ion exchange are better made by vapor phase chromatography, but, in general, ion exchange and vapor phase chromatography complement one another. It is precisely those compounds that do not respond to vapor phase chromatography that are best suited to ion exchange separation.

<sup>62</sup> Stein, W. H., and Moore, S., *Cold Spring Harbor Symposia Quant. Biol.*, **14**, 179, 1949; Moore, S., and Stein, W. H., *J. Biol. Chem.*, **192**, 663, 1951; Moore, S., and Stein, W. H., *ibid.*, **211**, 893, 907, 1954. See also chapter by P. B. Hamilton, in Calmon, C., and Kressman, T. R. E. (Eds.), *Ion Exchangers in Organic and Biochemistry*, Interscience Publishers, Inc., New York, 1957.

<sup>63</sup> Hamilton, P. B., and Anderson, R. A., *Anal. Chem.*, **31**, 1504, 1959.

<sup>64</sup> Hamilton, P. B., *Anal. Chem.*, **30**, 914, 1958.

<sup>65</sup> Schroeder, W. A., in Calmon, C., and Kressman, T. R. E. (Eds.), *Ion Exchangers in Organic and Biochemistry*, Interscience Publishers, Inc., New York, 1957.

<sup>66</sup> Cohn, W. E., *J. Am. Chem. Soc.*, **72**, 1471, 2811, 1950, also see Calmon, C., and Kressman, T. R. E. (Eds.), *Ion Exchangers in Organic and Biochemistry*, Interscience Publishers, Inc., New York, 1957.

<sup>67</sup> Schlenker, H. H., and Rieman, W., III, *Anal. Chem.*, **25**, 1637, 1953.

<sup>68</sup> Khym, J. X., and Zill, L. P., *J. Am. Chem. Soc.*, **73**, 2399, 1951; **74**, 2090, 1952, also see Calmon, C., and Kressman, T. R. E. (Eds.), *Ion Exchangers in Organic and Biochemistry*, Interscience Publishers, Inc., New York, 1957.

<sup>69</sup> Sherma, J., and Rieman, W., III, *Anal. Chim. Acta*, **18**, 214, 1958; **19**, 134, 1958; **20**, 357, 1959.

1. Gelatinous precipitates cannot be filtered.
2. Precipitates that cannot easily be dissolved out of the crucible sometimes cannot be filtered advantageously.
3. The crucibles, in the case of sintered glass crucibles, cannot be used at the elevated temperatures required for the ignition.
4. If the ignited residue required further treatment with a liquid reagent, a filter crucible may not be suitable.

For most filterable analytical precipitates, the use of filter crucibles, whether of sintered glass or sintered porcelain, is to be preferred over that of filter paper. For low-temperature application (under  $400^{\circ}\text{C}.$ ), the sintered glass crucibles may be employed; for temperatures up to  $1000^{\circ}\text{C}.$ , the sintered porcelain crucibles may be safely used. Gooch crucibles, owing to the difficulty in preparing the asbestos filter mat and drying to constant weight, are less preferred than the filter crucibles. However, for some determinations, they are perfectly satisfactory.

The precipitate and supernatant liquid are transferred to either a filter paper or filter crucible. This is done by first carefully decanting the supernatant liquid, taking care not to disturb the precipitate at the bottom of the beaker. The precipitate can then be washed, using a suitable wash liquid, by decantation, or transferred to the filtering device using as transfer aids a rubber policeman and a stream of wash liquid from a wash bottle. The nature of the precipitate determines whether or not it can be washed by decantation. Little advantage is obtained if the precipitate is composed of large crystalline particles. However, gelatinous precipitates which are difficult to filter may sometimes be washed free from soluble salts by this method. Of course the final washing is to be carried out on the filter.

**The Wash Liquid.**—The choice of wash liquid employed depends upon the nature of the precipitate. Such factors as the solubility of the precipitate in water, the solubility of the contaminating substance in water, the peptizability of the precipitate, and so on, will determine the composition of the wash liquid to be used.

If the precipitate is slightly soluble in water—and all are to a certain extent—a wash liquid should be employed which contains a cation or anion in common with the precipitate; i.e., the common-ion effect. Preferably, the substance added to the wash liquid should be ammonia, an ammonium salt, or an acid, because traces of these compounds remaining on the precipitate are easily volatilized during the ignition process and hence do not contaminate the final weighing form of the precipitate. An example of the use of such compounds in the wash liquids is dilute ammonium oxalate in the washing of calcium oxalate. Other examples, not employing the common-ion effect but necessary because the precipitates are too soluble to be washed in water or are easily hydrolyzed, are the use of dilute nitric acid to wash the silver halides and dilute ammonia to wash magnesium ammonium phosphate.

For precipitates containing a water-insoluble contaminate, such as an organic chelating agent used to precipitate an insoluble metal chelate, organic solvents may be employed. Such solvents as alcohol, acetone, ether, and others, are employed either as the pure solvent or mixed with water. In some cases, an acid is also added to the organic solvent-water mixture.

Perhaps the most difficult precipitates to wash are those that are gelatinous or are easily peptized. The wash liquid for these precipitates should contain an electrolyte, preferably an easily volatilized compound, such as ammonia, an ammo-

nium salt, or an acid. The type of electrolyte employed is immaterial as long as it does not alter the nature of the precipitate, either during the washing or drying process. Hydrous iron(III) oxide should be washed with an ammonium nitrate solution rather than ammonium chloride because the latter compound would form slightly volatile iron(III) chloride during the ignition process. Nonvolatile electrolytes would be unsuitable.

Whenever possible, the wash liquid should be used hot because of the decrease in viscosity of liquids at elevated temperatures resulting in more rapid filtration and also the increased solubility of the contaminants in hot solutions. However, inasmuch as the solubility of the precipitate also increases in hot solutions, cold wash liquids may have to be employed.

Several small portions of a wash liquid are better than a large one of the same volume. This is shown by the distribution law where the weight (in grams) of foreign substance in the solution adhering to the precipitate after washing,  $W_n$ , is equal to:<sup>2</sup>

$$W_n = \left( \frac{v}{V + v} \right)^n v C_0$$

where  $v$  is the volume (in milliliters) of liquid remaining with the precipitate after draining;  $V$  is the volume of wash liquid added each time;  $C_0$  is the concentration (in grams per milliliter) of soluble substances in the original solution; and  $n$  is the number of washings. The above expression was derived on the assumption that the foreign compound was simply mechanically associated with the precipitate. This is not always the case because of adsorption on the precipitate or isolation of the contaminant into the interior of the precipitate where it is not in contact with the wash liquid. As a general rule, six to ten washings are sufficient for most precipitates. If possible, the filtrate should be tested for the foreign substance after the last washing to determine if it is completely removed.

## DRYING AND IGNITION OF PRECIPITATES

To be useful for the analytical procedure, the precipitate, after proper washing should be converted into a suitable weighing form either by drying or ignition at elevated temperatures. The temperature limits for these processes will depend largely on the nature of the precipitate. Some precipitates, such as the aluminum 8-quinolinol chelate, may be either weighed after drying at 100° to 110°C.,<sup>3</sup> or ignited to aluminum oxide at 1000°C.<sup>4</sup> Still other precipitates, such as calcium oxalate, may be ignited and weighed either as calcium carbonate or as calcium oxide; the choice is up to the analyst. Some precipitates are of a nonstoichiometric composition and must be converted to a stoichiometric compound by ignition. The drying temperatures may vary from room temperature in a vacuum desiccator, such as is described for calcium picrolonate,<sup>5</sup> up to 200° to 300°C. Ignition temperatures up to 1200°C. or higher may be required for certain precipitates.

<sup>2</sup> Ibid., p. 255.

<sup>3</sup> Hollingshead, R. G. W., *Oxine and its Derivatives*, Butterworths, London, Vol. I, p. 98, 1954.

<sup>4</sup> Duval, C., *Inorganic Thermogravimetric Analysis*, Elsevier Publishing Co., Amsterdam, p. 120, 1953.

<sup>5</sup> Ibid., p. 159.

*Methods of Heating.*—If a choice is possible, drying in an electric oven containing a thermostat to maintain a constant temperature, or ignition in an electric muffle furnace, also thermostatically controlled, is preferred over that of open-burner flames or gas-heated equipment. The uncertainty in the temperatures attained as well as the lack of temperature control using gas flames is adequate reason to prefer electrical devices. If gas flames are to be used, the approximate temperatures attained by them are as follows: <sup>a</sup>

<i>Burner</i> <sup>a</sup>	<i>Crucible</i>	<i>Temperature, °C.</i>
Bunsen	Covered platinum	900–1050
Tirrill	Covered platinum	1050–1150
Meker	Covered platinum	1150–1250
Blast	Covered platinum	1100–1300
Tirrill	Covered porcelain in radiator	700
Meker	Covered porcelain in radiator	725–800
Blast	Covered porcelain in radiator	900

<sup>a</sup> Based on temperatures which were obtained with carbureted water gas having a heating value of 600 Btu per cu. ft.

As can be seen, the use of platinum crucibles for high-temperature flame ignitions is to be preferred over those made from porcelain, because of the higher temperatures attainable. However, this is not the case when they are used in an electric muffle furnace. It might be advantageous in the case of the latter to use porcelain crucibles for the ignition process because of the attack of platinum by various substances. It should also be emphasized that there is an appreciable loss in weight of platinum crucibles when heated for long periods above 1000°C. If used under these conditions, the weight change of an identical empty crucible should be determined under the conditions of the ignition.

It is permissible to ignite precipitates in filter paper provided that certain precautions are followed. Precipitates that are reduced by charred paper, such as lead sulfate to lead sulfide, and certain arsenates to volatile arsenic, should preferably be ignited in sintered porcelain crucibles. In some cases, however, the reduced part of the precipitate is oxidized back to its initial state by further heating at elevated temperatures in the presence of an air or oxygen atmosphere.

To ignite a precipitate contained on a paper filter, the paper and its contents are removed from the funnel, folded, and placed into the crucible. It is not recommended that the filter paper and contents be first dried in an electric oven at 100°C. before ignition because of the danger of precipitate loss when the dried paper is folded and placed into the crucible. However, this may be necessary in the case of certain hydrous oxides that contain large amounts of water. The crucible is then set in a vertical position on a triangle on a ring stand and heated with a burner using a small flame. The crucible should be loosely covered, care being taken that the contents do not spatter. After all of the moisture has been removed, the burner flame is increased to carbonize the paper. By no means should the paper be allowed to burst into flame. After the paper has been completely

<sup>a</sup> Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, John Wiley and Sons, New York, p. 107, 1953.

charred, the crucible is placed at a 45° angle to the triangle, the cover positioned so that the contents have access to air, and the crucible heated to red-heat to burn off the carbon. The crucible is then placed in a vertical position, covered, and ignited to the desired temperature for about 30 minutes. The exact final ignition period will depend on the character of the precipitate. It should be remembered that the atmosphere inside the crucible is not necessarily air but a mixture of nitrogen, water vapor, and combustion products. These gases limit the oxidation processes as well as elevate the dehydration and decomposition temperatures of certain hydrates and metal carbonates. Thus, longer ignition periods are generally preferred. The flame should not completely envelope the crucible, especially when readily reducible substances such as tin oxide are present. After the crucible has been ignited, it is allowed to cool slightly (to below red-heat) and then placed in a desiccator, over a suitable desiccant, to cool to room temperature. Generally, a cooling period of 30 minutes is satisfactory, although in cases where the residue is hygroscopic, a shorter period is more desirable.

A similar ignition process may be followed if an electric muffle furnace is to be used. After the carbon is burned off, the covered crucible is placed into a furnace and ignited to the desired ignition temperature.

If sintered porcelain crucibles are employed, the precipitates may be dried or ignited to any temperature up to about 1200°C. If the precipitate contains organic matter, and is to be ignited to a fairly high temperature, the crucible and contents should first be pre-ignited with a small burner flame to carbonize the contents. It is then ignited to the desired temperature as given above.

The drying and ignition temperatures of a precipitate are vitally important. The commonly used expression "ignite at red-heat" is inadequate in view of the advent of the modern automatic recording thermobalance, which can be used to define precisely the thermal stability of a precipitate. Indeed, any new analytical precipitate should be subjected to thermogravimetric examination to establish its thermal stability in regard to drying and ignition temperatures. Thermogravimetric examination may also reveal the presence of suitable intermediate weighing forms which would not be observable under normal procedures. In other cases, slight changes in the composition of a precipitate's weighing form are dependent on the temperature; hence, precise temperature control is required to obtain the required weighing form stoichiometry.

**Thermal Stability of Precipitates.**—The thermal stability of approximately 1000 well-known precipitates has been determined by Duval and co-workers<sup>7</sup> and others.<sup>8</sup> Some precaution should be exercised concerning the temperature limits since these were determined under nonequilibrium conditions and are dependent on the furnace heating rate, sample size, sample particle size, furnace atmosphere, etc.<sup>9</sup> The precipitate should not be dried or ignited at the extreme end of the thermal stability plateau but a temperature somewhere near the center of the plateau should be used.

The thermal stability of a number of precipitates are given in Table 11-1.

<sup>7</sup> Duval, C., *Inorganic Thermogravimetric Analysis*, Elsevier Publishing Co., Amsterdam, p. 120, 1953.

<sup>8</sup> Wendlandt, W. W., *Anal. Chem.*, 27, 1277, 1955; 28, 499, 1001, 1956; 29, 800, 1957; 30, 58, 61, 1958; 31, 408, 1959.

<sup>9</sup> Newkirk, A. E., *Anal. Chem.*, 32, 1558, 1960.



TABLE 11-1. THE THERMAL STABILITY OF CERTAIN ANALYTICAL PRECIPITATES %

Element	Precipitated by	Composition of Weighing Form	Thermal Stability Range, °C.
Ag	Electrolysis HCl HBr K <sub>2</sub> CrO <sub>4</sub>	Ag AgCl AgBr Ag <sub>2</sub> CrO <sub>4</sub>	<950 70-600 70-946 92-812
Al	Gaseous NH <sub>3</sub> 8-Quinolinol Bromine Na <sub>2</sub> HPO <sub>4</sub>	Al <sub>2</sub> O <sub>3</sub> Al(C <sub>9</sub> H <sub>6</sub> NO) <sub>3</sub> Al <sub>2</sub> O <sub>3</sub> AlPO <sub>4</sub>	>475 102-220 >280 >743
As	H <sub>2</sub> S Ca <sup>++</sup> Pb <sup>++</sup>	As <sub>2</sub> S <sub>3</sub> Ca <sub>2</sub> As <sub>2</sub> O <sub>7</sub> PbHAsO <sub>4</sub>	200-275 350-946 81-269
Au	Pyrogallol Thiophenol Thiophenol	Au C <sub>6</sub> H <sub>5</sub> SAu Au	20-957 <157 187-972
B	Boric acid K <sup>+</sup> Nitron	B <sub>2</sub> O <sub>3</sub> KBF <sub>4</sub> C <sub>20</sub> H <sub>16</sub> N <sub>4</sub> HBf <sub>4</sub>	443-946 50-410 50-197
Ba	H <sub>2</sub> SO <sub>4</sub> (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> K <sub>2</sub> CrO <sub>4</sub>	BaSO <sub>4</sub> BaO BaCrO <sub>4</sub>	780-1100 400-813 <60
Be	Aqueous NH <sub>3</sub> H <sub>2</sub> SO <sub>4</sub> Na <sub>2</sub> HPO <sub>4</sub>	BeO BeSO <sub>4</sub> Be <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	>900 346-679 640-951
Bi	Formaldehyde (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> H <sub>3</sub> AsO <sub>4</sub>	Bi BiPO <sub>4</sub> BiAsO <sub>4</sub>	73-150 379-961 47-400
Br	Ag <sup>+</sup>	AgBr	70-946
C	Ag <sup>+</sup> Cu <sup>++</sup> Ag <sup>+</sup>	AgCN Cu <sub>2</sub> (SCN) <sub>2</sub> Ag <sub>4</sub> [Fe(CN) <sub>6</sub> ]	93-237 103-298 60-229
Ca	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> Iodic acid Na <sub>2</sub> HAsO <sub>4</sub>	CaC <sub>2</sub> O <sub>4</sub> CaCO <sub>3</sub> CaO CaSO <sub>4</sub> Ca(IO <sub>3</sub> ) <sub>2</sub> Ca <sub>2</sub> As <sub>2</sub> O <sub>7</sub>	226-398 478-635 838-1025 105-890 106-540 350-946

TABLE 11-1. (Continued)

Element	Precipitated by	Composition of Weighing Form	Thermal Stability Range, °C.
Cd	KOH H <sub>2</sub> S 8-Quinolinol	CdO CdS Cd(C <sub>9</sub> H <sub>6</sub> NO) <sub>2</sub>	371-880 218-420 280-384
Ce	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	CeO <sub>2</sub>	>360
Cl	Ag <sup>+</sup>	AgCl	70-600
Co	Electrolysis (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> 8-Quinolinol K <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Co Co <sub>2</sub> P <sub>2</sub> O <sub>7</sub> Co(C <sub>9</sub> H <sub>6</sub> NO) <sub>2</sub> Co <sub>3</sub> O <sub>4</sub>	50-193 636-946 115-295 285-946
Cr	Aqueous NH <sub>3</sub> AgNO <sub>3</sub> 8-Quinolinol	Cr <sub>2</sub> O <sub>3</sub> Ag <sub>2</sub> CrO <sub>4</sub> Cr(C <sub>9</sub> H <sub>6</sub> NO) <sub>3</sub>	812-944 92-812 70-156
Cs	HCl HClO <sub>4</sub> Sodium tetraphenylboron	CsCl CsClO <sub>4</sub> Cs[B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]	110-877 42-543 <210
Cu	Electrolysis H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> 8-Quinolinol Salicylaldehyde Thionalide Anthranilic acid	Cu CuC <sub>2</sub> O <sub>4</sub> Cu(C <sub>9</sub> H <sub>6</sub> NO) <sub>2</sub> Cu(C <sub>7</sub> H <sub>6</sub> NO <sub>2</sub> ) <sub>2</sub> Cu(C <sub>12</sub> H <sub>10</sub> ONS) <sub>2</sub> Cu(NH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> ) <sub>2</sub>	<67 100-270 66-269 <150 148-167 <225
Dy	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Dy <sub>2</sub> O <sub>3</sub>	>745
Er	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Er <sub>2</sub> O <sub>3</sub>	>720
Eu	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Eu <sub>2</sub> O <sub>3</sub>	>620
F	CaCl <sub>2</sub> PbCl <sub>2</sub> BaCl <sub>2</sub>	CaF <sub>2</sub> PbClF BaSiF <sub>6</sub>	400-950 66-538 100-345
Fe	Aqueous NH <sub>3</sub> Cupferron 8-Quinolinol	Fe <sub>2</sub> O <sub>3</sub> Fe[C <sub>6</sub> H <sub>5</sub> (NO) <sub>2</sub> ] <sub>3</sub> Fe(C <sub>9</sub> H <sub>6</sub> NO) <sub>3</sub>	470-946 <98 <284
Ga	Aqueous NH <sub>3</sub> 5,7-Dibromo-8-quinolinol Cupferron	Ga <sub>2</sub> O <sub>3</sub> Ga(C <sub>9</sub> H <sub>4</sub> NOBr <sub>2</sub> ) <sub>3</sub> Ga <sub>2</sub> O <sub>3</sub>	408-946 100-224 >745
Gd	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Gd <sub>2</sub> O <sub>3</sub>	>700

TABLE 11-1. (Continued)

Element	Precipitated by	Composition of Weighing Form	Thermal Stability Range, °C.
Ge	(NH <sub>4</sub> ) <sub>2</sub> S Tannin Molybdic acid and 8-quinolol	GeO <sub>2</sub> GeO <sub>2</sub> (C <sub>9</sub> H <sub>6</sub> NOH) <sub>4</sub> · (GeO <sub>2</sub> ·12MoO <sub>3</sub> )	410-946 900-950 50-115
Hf	Aqueous NH <sub>3</sub> Mandelic acid	HfO <sub>2</sub> Hf(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OCO <sub>2</sub> ) <sub>4</sub>	350-660 90-260
Hg	Electrolysis (NH <sub>4</sub> ) <sub>2</sub> S K <sub>2</sub> CrO <sub>4</sub> Na <sub>2</sub> HAsO <sub>4</sub> Thionalide	Hg HgS Hg <sub>2</sub> CrO <sub>4</sub> Hg <sub>3</sub> (AsO <sub>4</sub> ) <sub>2</sub> Hg(C <sub>12</sub> H <sub>10</sub> ONS) <sub>2</sub>	<70 <109 52-256 45-418 90-169
Ho	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Ho <sub>2</sub> O <sub>3</sub>	>735
I	AgNO <sub>3</sub> AgNO <sub>3</sub>	AgIO <sub>3</sub> AgI	80-410 60-900
In	Aqueous NH <sub>3</sub> 8-Quinolol H <sub>2</sub> S	In <sub>2</sub> O <sub>3</sub> In(C <sub>9</sub> H <sub>6</sub> NO) <sub>3</sub> In <sub>2</sub> S <sub>3</sub>	345-880 100-285 94-221
Ir	2-Mercaptobenzothiazole	Ir	520-980
K	HCl HClO <sub>4</sub> Dipicrylamine Sodium tetraphenylboron	KCl KClO <sub>4</sub> KC <sub>12</sub> H <sub>4</sub> O <sub>12</sub> N <sub>7</sub> K[B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]	219-813 73-653 50-220 <265
La	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	La <sub>2</sub> O <sub>3</sub>	>800
Lu	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Lu <sub>2</sub> O <sub>3</sub>	>715
Mg	NaOH NH <sub>4</sub> F H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> 8-Quinolol	MgO MgF <sub>2</sub> MgC <sub>2</sub> O <sub>4</sub> Mg(C <sub>9</sub> H <sub>6</sub> NO) <sub>2</sub>	>800 411-816 233-397 88-300
Mn	KOH K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> K <sub>2</sub> C <sub>2</sub> O <sub>4</sub> 8-Quinolol	Mn <sub>3</sub> O <sub>4</sub> MnC <sub>2</sub> O <sub>4</sub> Mn <sub>3</sub> O <sub>4</sub> Mn(C <sub>9</sub> H <sub>6</sub> NO) <sub>2</sub>	>946 100-214 670-943 117-250
Mo	Aqueous NH <sub>3</sub> H <sub>2</sub> S 8-Quinolol	MoO <sub>3</sub> MoO <sub>3</sub> MoO <sub>2</sub> (C <sub>9</sub> H <sub>6</sub> NO) <sub>2</sub>	344-782 485-780 40-270

TABLE 11-1. (Continued)

Element	Precipitated by	Composition of Weighing Form	Thermal Stability Range, °C.
N	Nitron Sodium tetraphenylboron Chloroplatinic acid	$C_{20}H_{16}N_4HNO_3$ $NH_4[B(C_6H_5)_4]$ $(NH_4)_2[PtCl_6]$	20-242 <130 <181
Na	$HClO_4$ $Zn(C_2H_3O_2)_2$ and $UO_2(C_2H_3O_2)_2$	$NaClO_4$ $\frac{1}{2}Na_2U_2O_7 \cdot ZnU_2O_7$	130-471 360-674
Nb	Cupferron 8-Quinolinol	$Nb_2O_5$ $Nb_2O_5$	650-950 649-800
Nd	$H_2C_2O_4$	$Nd_2O_3$	>735
Ni	Electrolysis NaOH $H_2C_2O_4$ 8-Quinolinol Dimethylglyoxime	Ni NiO NiO $Ni(C_9H_6NO)_2$ $NiC_8H_{14}O_4N_4$	<93 250-815 633-845 100-232 79-172
P	$(NH_4)_2MoO_4$ 8-Quinolinol	$(NH_4)_2H-$ $[P(Mo_3O_{10})_4] \cdot H_2O$ $(C_9H_7NO)_3H_3(PMo_{12}O_{40})$	160-415 85-285
Pb	HCl $H_2SO_4$ $(NH_4)_2HPO_4$ Thionalide Salicylaldoxime	$PbCl_2$ $PbSO_4$ $Pb_2P_2O_7$ $Pb(C_{12}H_{10}NS)_2$ $Pb(C_7H_5NO)_2$	53-528 271-959 358-880 71-134 45-180
Pd	Ethylene Dimethylglyoxime o-Phenanthroline	Pd $Pd(C_4H_7O_2N_2)_2$ $PdCl_2 \cdot C_{12}H_5N_2$	<384 45-171 50-389
Pr	$H_2C_2O_4$	$Pr_6O_{11}$	>790
Pt	$NH_4Cl$	$(NH_4)_2[PtCl_6]$	<181
Rb	$HClO_4$ Chloroplatinic acid Sodium tetraphenylboron	$RbClO_4$ $Rb_2[PtCl_6]$ $Rb[B(C_6H_5)_4]$	101-343 70-674 <240
Re	Nitron	$C_{20}H_{16}N_4HReO_4$	91-288
S	$AgNO_3$ Benzidine	$Ag_2S$ $C_{12}H_{12}N_2 \cdot H_2SO_4$	69-615 72-130
Sb	$H_2S$	$Sb_2S_3$	176-275

TABLE 11-1. (Continued)

Element	Precipitated by	Composition of Weighing Form	Thermal Stability Range, °C.
Sc	8-Quinolinol Aqueous $\text{NH}_3$ $\text{H}_2\text{C}_2\text{O}_4$	$\text{Sc}(\text{C}_9\text{H}_6\text{NO})_3 \cdot \text{C}_9\text{H}_6\text{NOH}$ $\text{Sc}_2\text{O}_3$ $\text{Sc}_2\text{O}_3$	<125 542-946 >635
Se	$\text{SO}_2$ $\text{Pb}(\text{NO}_3)_2$	Se $\text{PbSeO}_4$	<370 <330
Si	HCl KF Pyramidone + molybdic acid	$\text{SiO}_2$ $\text{K}_2\text{SiF}_6$ $\text{SiO}_2 \cdot 12\text{MoO}_3$	358-946 60-410 399-787
Sm	$\text{H}_2\text{C}_2\text{O}_4$	$\text{Sm}_2\text{O}_3$	>735
Sn	Aqueous $\text{NH}_3$ Cupferron	$\text{SnO}_2$ $\text{SnO}_2$	>834 >747
Sr	$\text{H}_2\text{SO}_4$ Iodic acid $\text{K}_2\text{C}_2\text{O}_4$	$\text{SrSO}_4$ $\text{Sr}(\text{IO}_3)_2$ $\text{SrC}_2\text{O}_4$	100-300 157-600 177-400
Ta	Tartaric acid Cupferron	$\text{Ta}_2\text{O}_5$ $\text{Ta}_2\text{O}_5$	>894 >1000
Tb	$\text{H}_2\text{C}_2\text{O}_4$	$\text{Tb}_4\text{O}_7$	>725
Tc	$\text{N}_2\text{H}_4$	Tc	<40
Th	Gaseous $\text{NH}_3$ 8-Quinolinol $\text{H}_2\text{C}_2\text{O}_4$	$\text{ThO}_2$ $\text{Th}(\text{C}_9\text{H}_6\text{NO})_4 \cdot \text{C}_9\text{H}_6\text{NOH}$ $\text{ThO}_2$	472-945 <80 610-946
Ti	Aqueous $\text{NH}_3$ 5,7-Dichloro-8-quinolinol	$\text{TiO}_2$ $\text{TiO}(\text{C}_9\text{H}_4\text{NOCl}_2)_2$	350-946 105-195
Tl	HCl $\text{K}_2\text{CrO}_4$ Tetraphenylarsonium chloride	$\text{TlCl}$ $\text{TlCrO}_4$ $(\text{C}_6\text{H}_5)_4\text{AsTlCl}_4$	56-425 97-745 50-218
Tm	$\text{H}_2\text{C}_2\text{O}_4$	$\text{Tm}_2\text{O}_3$	>730
U	Aqueous $\text{NH}_3$ 8-Quinolinol $\text{H}_2\text{C}_2\text{O}_4$	$\text{UO}_3$ $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_6\text{NOH}$ $\text{U}_4\text{O}_8$	480-610 <150 700-946

TABLE 11-1. (Continued)

Element	Precipitated by	Composition of Weighing Form	Thermal Stability Range, °C.
V	Aqueous $\text{NH}_3$ Cupferron	$\text{V}_2\text{O}_5$ $\text{V}_2\text{O}_5$	448-951 581-946
W	8-Quinolinol Acridine $\text{Pb}^{++}$	$\text{WO}_3$ $\text{WO}_3$ $\text{PbWO}_4$	>674 >812 >100
Y	$\text{H}_2\text{C}_2\text{O}_4$	$\text{Y}_2\text{O}_3$	>735
Yb	$\text{H}_2\text{C}_2\text{O}_4$	$\text{Yb}_2\text{O}_3$	>730
Zn	Electrolysis Aqueous $\text{NH}_3$ $(\text{NH}_4)_2\text{HPO}_4$ 8-Quinolinol	Zn ZnO $\text{Zn}_2\text{P}_2\text{O}_7$ $\text{Zn}(\text{C}_9\text{H}_6\text{NO})_2$	<54 >1000 610-946 127-284
Zr	Aqueous $\text{NH}_3$ <i>p</i> -Bromomandelic acid Mandelic acid	$\text{ZrO}_2$ $\text{Zr}(\text{BrC}_8\text{H}_6\text{O}_3)_4$ $\text{Zr}(\text{C}_8\text{H}_7\text{O}_3)_4$	400-1000 <150 60-188

## Chapter 12

# TITRATION METHODS

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### FUNDAMENTAL CONSIDERATIONS<sup>1</sup>

**Requirements.**—For application of a titrimetric method, the chemical process involved should consist of a single, rapid stoichiometric reaction between the substance titrated and the standard solution used as the titrant. The end point is detected by an indicator which shows a marked change in some property (color, potential of an electrode system, etc.) of the titration system; this change should coincide with the stoichiometric point of the titration reaction.

**Primary Standards.**—A primary standard should be a pure substance (assay usually 99.95 to 100.05%) or one of known purity with respect to the active component; it should be stable in storage, at oven temperatures for drying, and during weighing. A high equivalent weight is desirable to minimize weighing errors. Several primary standards are available from the National Bureau of Standards and from chemical supply houses. Several substances of analytical reagent grade are sufficiently pure to serve as primary standards for ordinary work, or they may be made so by recrystallization.

**Standard Solutions.**—Some standard solutions may be prepared directly from a primary standard by diluting an accurately weighed amount of the solute to a known volume. Many of the solutes required in titration methods are not available as primary standards; for this reason, or for reasons of economy, many titrants are made to the approximate concentration desired, using rough weight and volume measurements, the solution is then standardized by titrating accurately weighed samples of a suitable primary standard. A solution of exactly predetermined normality, e.g., 0.1000 *N*, or an exact titer in terms of a certain desired constituent, e.g., silver nitrate having a chloride titer of 0.0050 g. per ml., is most easily prepared by the direct method, if the appropriate primary standard is available. Alternatively, an approximate solution may be prepared of slightly higher than the desired concentration, after standardization the solution may be diluted volumetrically to the desired normality or titer. Some laboratories choose the concentration of the titrant so that each milliliter represents a convenient integral per cent of desired constituent when a certain sample weight is taken.

**End-Point Detection.**—End-point detection by various "instrumental" methods (potentiometric, conductometric, etc.) is beyond the scope of this treatment; only

<sup>1</sup> For a discussion of theoretical fundamentals, consult Kolthoff, I. M., and Stenger, W. A., *Volumetric Analysis*, Vol. I, Interscience Publishers, Inc., New York, 1942.

the visual methods will be treated. Owing to the variety of types of titrimetric methods and indicator actions, the subject of indicator action will be treated in conjunction with the types of methods or with specific determinations.

In titrimetric analysis the sample (primary standard, or sample for analysis) should be large enough that weighing errors are not significant, but not so large as to require refilling of the buret. Also, the volume of titrant solution used should be large enough that volumetric errors are not significant; when a 50-ml. buret is used, about 40 ml. or more would be required to keep the volumetric errors within 0.1% or one part per thousand. Because a finite amount of titrant is required to give the indicator action, and because the indicator change may not occur exactly at the stoichiometric point, a blank should be determined and subtracted from the volume of solution used in the titration; however, if the titrant has been standardized by the same reaction as is involved in the analysis at hand, the indicator error largely cancels out and no blank correction is necessary.

**Calculations.**—The calculations of titrimetric analysis are usually based on normality and equivalent weight, or on titer. A one normal (1 N) solution contains one gram equivalent weight of solute, for a given type of reaction, per liter of solution. When a series of reactions is involved in an analysis, the equivalent weight of the desired constituent is based upon the reaction in which the standard solution is used. The titer of a solution is the weight of substance contained in, or of another substance that can be titrated by, 1.00 ml. of a given standard solution. When many similar analyses are to be performed, "factor-volume" samples and solutions are often used, so that there is a simple integral relation between volume of standard solution used and per cent of desired constituent. An excellent treatment of titrimetric calculations is given by Hamilton and Simpson.<sup>2</sup>

**Types of Reaction and Equivalency.**—The equivalent weight of a substance is that weight of substance which, in the reaction that occurs, furnishes, reacts with, or is chemically equivalent to one gram-atom of:

- a. Hydrogen ions or protons (neutralization methods);
- b. Univalent cation in a precipitate, weak ionogen, or complex formed (precipitation and complexation methods).
- c. Electrons transferred (oxidation-reduction methods).

## NEUTRALIZATION METHODS (ACIDIMETRY, ALKALIMETRY) <sup>3</sup>

### INDICATORS <sup>4</sup>

**Selection and Use of an Indicator.**—In acid-base titrations the solution undergoes a rapid change of hydrogen ion concentration or pH ( $\text{pH} = -\log[\text{H}^+]$ ) around the equivalence point; this point is ascertained by means of an indicator. Indicators are weakly ionized organic acids or bases that show markedly different colors in the ionized and nonionized forms. Different indicators show their color changes in different pH regions, but the color transition occurs over a pH range of about

<sup>2</sup> Hamilton, L. F., and Simpson, S. G., *Calculations of Analytical Chemistry*, 6th Ed., Chaps. 11–14, McGraw-Hill Book Co., Inc., New York, 1960.

<sup>3</sup> For a detailed discussion, see Kolthoff, I. M., and Stenger, W. A., *Volumetric Analysis*, Vol. II, Interscience Publishers, Inc., New York, 1947.

<sup>4</sup> See Clark, W. M., *The Determination of Hydrogen Ions*, 3rd Ed., Williams and Wilkins Co., Baltimore, 1928; Kolthoff, I. M., and Rosenblum, C., *Acid-Base Indicators*, The Macmillan Co., New York, 1937.



stants are sufficiently different (pK values different by about 4 units), and the indicators are chosen properly. For example, phosphoric acid,  $\text{H}_3\text{PO}_4$ , titrated with sodium hydroxide shows its first equivalence point at pH 4.7, in the color change interval of bromcresol green or methyl red; the second equivalence point occurs at pH 9.6, and a suitable indicator is thymol blue, phenolphthalein, or thymolphthalein.

Often a sharper color change can be achieved by the use of a mixed indicator, in which one indicator color is masked or screened by a second substance of complementary color; the intermediate color is therefore a neutral gray. The second substance may be a dye which is insensitive to pH, or another indicator of nearly the same pH interval and having an overlapping color complementary to the first indicator. Mixed indicators are especially useful when titration to a definite pH is required.

Many of the acid-base indicators are quite insoluble in water; they may be dissolved in alcohol, or rendered water soluble by conversion to sodium salts or chlorides by grinding the dry dye with the required amount of sodium hydroxide or hydrochloric acid, and then diluting to the appropriate volume.<sup>6</sup> Water-soluble indicators are available commercially<sup>7</sup> and are a great convenience.

The transition range and colors of indicators may be affected by temperature, concentration of neutral salts in solution, presence of nonaqueous solvents, and concentration of indicator; the last effect is particularly pronounced with one-color indicators such as phenolphthalein and thymolphthalein. In some cases and for high accuracy work, it is advisable to prepare a comparison solution of composition closely approximating that of the final titrated solution and containing the same amount of indicator, and to titrate the unknown solution to the same color tint.

**Preparation of Indicator Solutions.**—The indicators most often used in neutralimetry have their color transitions in the pH range of about 3 to 10. If water-soluble indicators<sup>7</sup> are used, prepare the solutions according to directions furnished by the supplier. Otherwise, prepare as given below.

Methyl yellow: 0.10% solution in 95% alcohol

Methyl orange: 0.20% solution in hot water; cool, and filter if necessary

Bromcresol green: 0.10% solution in 20% alcohol

Methyl red: 0.20% solution in hot water; cool, and filter if necessary

Chlorophenol red: 0.10% solution in 20% alcohol

Bromcresol purple: 0.10% solution in 95% alcohol

Bromthymol blue: 0.10% solution in 20% alcohol

Phenol red: 0.10% solution in 20% alcohol

Neutral red: 0.10% solution in 60% alcohol

Cresol red: 0.10% solution in 20% alcohol

Thymol blue: 0.10% solution in 20% alcohol; heat if necessary to dissolve

Phenolphthalein: 1.0% solution in 80% alcohol

Thymolphthalein: 0.10% solution in 95% alcohol

**Mixed Indicators.**—A number of common mixed indicators and their characteristics are:

Modified methyl orange: dissolve 0.40 g. of methyl orange and 0.56 g. of xylene cyanole FF in 100 ml. of alcohol and dilute with 100 ml. of water. Alkaline color, green; acid color, violet; neutral gray at pH 3.8 to 4.1.

Methyl purple or screened methyl red: dissolve 0.100 g. of methyl red in 50 ml.

<sup>6</sup> Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd Ed., John Wiley and Sons, New York, p. 170, 1953.

<sup>7</sup> Hartman-Leddin Co., Philadelphia, Pa.

TABLE 12-1. ACID-BASE INDICATORS <sup>a</sup>

Common Name	pH Interval	Acid Color	Alkaline Color
Cresol red <sup>a</sup> . . . . .	0.2-1.8	Red	Yellow
Thymol blue <sup>a</sup> , . . . . .	1.2-2.8	Red	Yellow
Methyl yellow . . . . .	2.8-4.0	Red	Yellow
Bromphenol blue . . . . .	3.0-4.6	Yellow	Purple
Methyl orange . . . . .	3.1-4.4	Red	Yellow
Bromcresol green . . . . .	3.8-5.4	Yellow	Blue
Methyl red . . . . .	4.2-6.2	Red	Yellow
Chlorphenol red . . . . .	4.8-6.4	Yellow	Red
Bromcresol purple . . . . .	5.2-6.8	Yellow	Purple
Bromthymol blue . . . . .	6.0-7.6	Yellow	Blue
Phenol red . . . . .	6.4-8.0	Yellow	Red
Neutral red . . . . .	6.8-8.0	Red	Yellow-brown
Cresol red <sup>b</sup> . . . . .	7.2-8.8	Yellow	Red
Cresol purple <sup>b</sup> . . . . .	7.4-9.0	Yellow	Purple
Thymol blue <sup>b</sup> . . . . .	8.0-9.6	Yellow	Blue
Phenolphthalein . . . . .	8.0-9.8	Colorless	Red-violet
Thymolphthalein . . . . .	9.3-10.5	Colorless	Blue
Alizarin yellow . . . . .	10.1-12.0	Yellow	Violet

<sup>a</sup> Acid range; the indicator has two color change intervals.

<sup>b</sup> Alkaline range; the indicator has two color change intervals.

1.5 to 2 units. The pH interval and colors of some common indicators are given in Table 12-1. The pH of the solution at the equivalence point in a neutralization titration depends on the degree of ionization of the acid and base involved in the reaction. If both acid and base are highly ionized, the equivalence point pH is 7.0, and one drop of dilute titrant may cause the pH to change from about 4 to 10 (when acid is titrated with base); any one of several different indicators can therefore be used. In the titration of a weak acid, e.g., acetic, benzoic, etc., by strong base, the solution at the equivalence point is alkaline (pH greater than 7), the exact pH depending upon the ionization constant of the acid and the concentration of the anion (salt) in the final solution. Similarly, the solution is slightly acidic (pH less than 7) at the equivalence point in the titration of a weak base by a strong acid. Therefore, when the substance titrated is a weak acid or a weak base, an indicator must be chosen that has its color transition at a pH which coincides with, or lies very close to, the equivalence point pH; large errors would otherwise occur.

Stepwise titration of polyprotic acids (e.g., phosphoric acid) and/or their alkali salts (e.g., phosphate, carbonate, etc.) is possible if the successive ionization con-

<sup>a</sup> Taken from Ayres, G. H., *Quantitative Chemical Analysis*, p. 355, Harper and Brothers, New York, 1958. Used by permission of the publisher.

stants are sufficiently different (pK values different by about 4 units), and the indicators are chosen properly. For example, phosphoric acid,  $\text{H}_3\text{PO}_4$ , titrated with sodium hydroxide shows its first equivalence point at pH 4.7, in the color change interval of bromcresol green or methyl red; the second equivalence point occurs at pH 9.6, and a suitable indicator is thymol blue, phenolphthalein, or thymolphthalein.

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<sup>7</sup> Hartman-Leddon Co., Philadelphia, Pa.

of alcohol; dissolve 0.050 g. of methylene blue in 50 ml. of alcohol; mix the two solutions and store in an amber bottle. Alkaline color, green; acid color, violet; neutral gray at pH 5.2.

Mix 0.1% solutions of cresol red and thymol blue in a 1:3 volume ratio. Acid color, yellow; alkaline color (above pH 8.4), violet; pink at pH 8.2.

Mix 0.1% solutions of phenolphthalein and methyl green in a 1:2 volume ratio. Acid color, green; alkaline color (above pH 9), violet; pale blue at pH 8.8.

## STANDARD ACIDS

### HYDROCHLORIC ACID

Hydrochloric acid is the most commonly used titrant in acidimetry. Dilute solutions can be boiled for moderate periods without loss of HCl. Standard solutions are usually prepared at approximately the desired concentration and then standardized. A direct stock standard solution (approximately 6 *N*) can be prepared as the constant boiling solution, and diluted quantitatively to lower concentrations for use.

*Preparation of Approximate 0.1 N Solution (HCl, mol. wt. and equiv. wt. = 36.465).*—A 0.1 *N* solution contains 3.65 g. of HCl per liter. Analytical reagent grade concentrated hydrochloric acid has a specific gravity of about 1.18, contains about 36% by weight of HCl, and is about 12 *N*. Preparation of a liter of 0.1 *N* solution requires about 8.5 ml. of the concentrated acid. For each liter of 0.1 *N* solution to be prepared, rough measure (graduate) 9 ml. of concentrated acid and dilute with water to approximately the desired volume; mix thoroughly before standardizing.

*Standardization.* a. Against Sodium Carbonate ( $\text{Na}_2\text{CO}_3$ , mol. wt. = 106.00; equiv. wt. for complete neutralization = 53.00).—Analytical reagent grade sodium bicarbonate may be recrystallized, if necessary, by directions given by Hillebrand et al.<sup>8</sup> Convert the bicarbonate to carbonate as follows: Place the purified sodium bicarbonate in a platinum crucible, heat in a sand bath to 260° to 290°C., with the thermometer bulb in the solid, for 30 to 60 minutes, with occasional stirring. Transfer the crucible and contents to a weighing bottle, cool in a desiccator, and weigh. Repeat the heating, to constant weight. Accurately weigh out samples of the pure, dry sodium carbonate appropriate for the normality of the acid to be standardized; for approximately 0.1 *N* solution and assuming about 40 ml. for the titration, take samples of 0.2 to 0.25 g. Dissolve the sample in about 60 ml. of distilled water, add two drops of modified methyl orange (or methyl purple) indicator, and titrate with the acid to the neutral gray or very faint violet tint. Boil the solution for 1 minute to remove carbon dioxide (the solution should return to the green color), cool, and complete the titration dropwise to the neutral gray or first faint violet tint. Calculate the normality of the acid:

$$N = \frac{\text{g. Na}_2\text{CO}_3 \text{ taken}}{\text{Ml. acid used} \times 0.05300}$$

b. Against Borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , mol. wt. = 381.42; equiv. wt. = 190.71).—Borax is readily prepared in high purity and of exact hydrate composition by re-

<sup>8</sup> Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd Ed., John Wiley and Sons, New York, p. 176, 1953.

crystallization from water below 55°C. (to prevent separation of crystals of the pentahydrate). The decahydrate is stable at room temperature at relative humidity from about 40 to 99%; it is stored in a desiccator over saturated solution of sodium bromide, or saturated sodium chloride and sucrose solution. Borax has the advantage of a high equivalent weight:  $B_4O_7 = + 2H^+ + 5H_2O \rightarrow 4H_3BO_3$ . The theoretical end point pH is approximately 5. For standardization of 0.1 *N* solution, accurately weigh about 0.8 g. of borax, dissolve it in about 60 ml. of distilled water, add two drops of methyl red indicator, and titrate to the first detectable color change from yellow to red-orange.

c. Against Standard Sodium Hydroxide Solution.—A solution of carbonate-free sodium hydroxide that has been standardized can be used for standardizing an acid by performing a comparison titration. The titration should be made in the same direction and with the same indicator as was used in the standardization; for example, if the sodium hydroxide was standardized against potassium acid phthalate (as described later), using phenolphthalein indicator, an accurately measured volume of the acid to be standardized is titrated with the standard sodium hydroxide to the first pink tinge of phenolphthalein.

*Preparation of Constant Boiling Hydrochloric Acid.*—A stock supply of standard (approximately 6 *N*, known to five significant figures) can be prepared by distilling a 1:1 hydrochloric acid, discarding the first three-fourths of the distillate, and collecting the next 15% or so of the constant boiling acid; the barometric pressure at the time of distillation must be noted. Details of apparatus and procedure have been published.<sup>9,10</sup> The composition of the constant boiling acid varies with the pressure of distillation, as shown in Table 12-2. The constant boiling acid is

TABLE 12-2. CONSTANT BOILING HYDROCHLORIC ACID

Pressure, mm. of Hg	Boiling Point, °C.	Density at 25°C.	% HCl by Weight	Grams for 1 Liter of 0.1000 <i>N</i> Soln.
770	108.584	1.0959	20.197	18.041
760			20.222	18.019
750			20.245	17.998
740	107.859	1.0962	20.269	17.977
730			20.293	17.956
700	106.424	1.0966	20.360	17.910

easily stored; it is not hygroscopic, and its composition is not changed by evaporation. For preparation of dilute solution for use as a titrant, the constant boiling acid is weighed accurately from a weight buret and diluted to volume in a volumetric flask. The weight of the acid required to prepare 1 liter of exact 0.1000 *N* solution is shown in the last column of Table 12.2.

<sup>9</sup> Foulk, C. W., and Hollingsworth, M., J. Am. Chem. Soc., 45, 1220 (1923).  
<sup>10</sup> Bonner, W. D., and Wallace, R. E., *ibid.*, 52, 1747 (1930).

## SULFURIC ACID

If a moderately concentrated solution of acid must be boiled without loss, sulfuric acid has the advantage over hydrochloric acid. Sulfuric acid is usually prepared at the approximate concentration needed, then standardized. Constant boiling sulfuric acid varies in composition only slightly with distillation pressure; at 750 mm. the constant boiling mixture contains 98.48%  $\text{H}_2\text{SO}_4$  by weight;<sup>11</sup> for use as a concentrated stock standard solution, however, storage presents a problem because of its high hygroscopicity. Sulfuric acid of about 52% by weight is in equilibrium with air of "ordinary" moisture content; thus it presents no storage problem; its exact composition can be determined from an accurate density measurement and reference to tables,<sup>12</sup> solutions for use as a titrant are prepared as needed by weighing the desired quantity from a weight buret and diluting to known volume. Alternatively, an aliquot of the stock solution can be standardized against an appropriate alkaline primary standard, and quantitative dilutions made for use as needed.

**Preparation of Approximate Solution ( $\text{H}_2\text{SO}_4$ , mol. wt. = 98.08; equiv. wt. = 49.04).**—Analytical reagent concentrated sulfuric acid has a specific gravity of about 1.84, contains about 96% by weight of  $\text{H}_2\text{SO}_4$ , and is about 36 N. Preparation of a liter of approximately 0.1 N solution requires about 3 ml. of the concentrated acid. *Pour the acid into a large volume of water—never the reverse—and dilute to the required volume; mix thoroughly.*

**Standardization.**—Follow the same procedure as for hydrochloric acid.

## STANDARD ALKALIES

Most alkalimetric titrations are made with sodium hydroxide solution. The solid reagent chemical contains more or less carbonate, and the solutions absorb carbon dioxide from the air to form carbonate. When used for the titration of weak acids, the carbonate makes the end points less distinct and results in an appreciable titration error.

Alkaline solutions should be stored in bottles of resistance glass or, preferably, of polyethylene. If the solution is to be maintained carbonate-free, the bottle should be fitted with a siphon delivery tube and the air inlet should be protected with a trap containing concentrated sodium hydroxide solution, or with a guard tube containing soda lime or soda asbestos.

Alkaline solutions that are to be used in the presence of carbon dioxide are best standardized against a standard acid solution, such as a diluted constant boiling hydrochloric acid, or acid that has been standardized against sodium carbonate. Carbonate-free solutions that are to be used with indicators having a high pH transition interval (e.g., phenolphthalein) should be standardized against potassium acid phthalate or benzoic acid.

## SODIUM HYDROXIDE

**Preparation of Ordinary Solution ( $\text{NaOH}$ , mol. wt. and equiv. wt. = 40.00).**—For approximately 0.1 N solution, dissolve about 5 g. of solid reagent in 100 to 200 ml. of distilled water, with constant stirring to prevent caking of the solid; dilute to about 1 liter and mix well. Standardize by titrating a measured volume of the

<sup>11</sup> Kunzler, J. E., *Anal. Chem.*, 25, 93 (1953).

<sup>12</sup> This book, pages 612-614.

solution with standard hydrochloric acid or sulfuric acid, using modified methyl orange or methyl purple indicator, as described under standardization of hydrochloric acid against sodium carbonate.

**Preparation of Carbonate-free Solution.** a. **From Concentrated NaOH Solution.**—Sodium carbonate is insoluble in sodium hydroxide solution of about 50% concentration. To 100 g. of sodium hydroxide pellets add 100 ml. of distilled water, stirring constantly until all the solid has dissolved. Transfer the solution to a large Pyrex test tube, close the tube with a stopper covered with tin foil, and allow the sodium carbonate to settle; centrifugation will hasten the settling. Siphon or pipet off the required amount of the clear solution (about 8 ml. of each liter of 0.1 *N* solution to be prepared) into the storage container, and dilute at once with distilled water that has been recently boiled and then cooled in a stoppered flask; mix thoroughly. Alternatively, the concentrated sodium hydroxide solution can be filtered through a fritted glass crucible, protected from carbon dioxide of the air; for a diagram of the apparatus, see Hillebrand.<sup>13</sup> Fit the storage bottle with a siphon delivery tube and a carbon dioxide guard on the air inlet.

b. **By Use of Anion Exchange Resin.**—Pass the sodium hydroxide solution containing carbonate through a column containing the chloride form of a strong base anion exchange resin (Amberlite IRA-400 or Dowex 1 or 2), which retains the carbonate. If chloride is objectionable in the solution, discard the first portions of effluent until a negative test for chloride is obtained. The resin can be regenerated by passing dilute hydrochloric acid through the column, followed by water until the excess acid is removed.

A direct standard solution of alkali hydroxide can be prepared from a weighed amount of pure sodium chloride or potassium chloride. Pass the chloride solution through a column containing a strong base anion exchange resin in the hydroxide form; wash the column well with water, and dilute the effluent solution and washings to known volume. After use, the resin can be regenerated with sodium hydroxide solution.

**Standardization.** a. **Against Potassium Acid Phthalate ( $C_6H_4(COOK)(COOH)$ , or  $KHC_8H_4O_4$ , mol. wt. and equiv. wt. = 204.22).**—Potassium acid phthalate, recommended as the primary standard for strong bases, is available commercially and from National Bureau of Standards. It is not hygroscopic, it is stable up to 135°C., and it is water soluble. Oven-dry the primary standard potassium acid phthalate at 115° to 120°C. for 1 to 2 hours; store in a weighing bottle in a desiccator. Accurately weigh the appropriate amount of the solid (for standardizing 0.1 *N* alkali, take about 0.8 g.), dissolve it in about 75 ml. of carbon dioxide-free distilled water, add three drops of phenolphthalein indicator, and titrate with the sodium hydroxide solution to the first faint permanent pink tinge. Run a blank on the same end volume of carbon dioxide-free water and indicator; subtract the blank from the volume of alkali used in the titration, and calculate the normality of the alkali. If higher accuracy is required, purge the titration flask from carbon dioxide (by sweeping with carbon dioxide-free air or with nitrogen) before use and during the titration.

b. **Against Benzoic Acid ( $C_6H_5COOH$  or  $HC_7H_5O_2$ , mol. wt. and equiv. wt. = 122.12).**—National Bureau of Standards supplies benzoic acid as a calorimetric

<sup>13</sup> Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd Ed., John Wiley and Sons, New York, p. 179, 1953.

standard; it is also suitable as a primary standard for alkali. Its principal disadvantage is its low solubility in water. Accurately weigh (about 0.5 g. for use with 0.1 N alkali) the pure dry benzoic acid, dissolve it in 10 ml. of 95% alcohol, dilute with about 40 ml. of carbon dioxide-free water, add three drops of phenolphthalein indicator, and titrate with the alkali to the first faint but permanent tinge. Run a blank consisting of 10 ml. of alcohol, carbon dioxide-free water to equal the end volume in the titration, and indicator. From the net volume of alkali, calculate its normality. For very exact work, carry out the titration in a carbon dioxide-free atmosphere.

### BARIUM HYDROXIDE

Barium hydroxide solution is automatically kept free from carbonate, due to the insolubility of barium carbonate in water and alkaline solutions. Its principal disadvantage is the insolubility of barium salts of many anions, such as sulfate and phosphate. When large amounts of solution are required, it is convenient to prepare a stock supply of saturated solution in contact with a large excess of solid  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . If the temperature remains constant, the concentration of solution remains constant even if carbon dioxide is absorbed. The saturated solution is about 0.35 N, which is more concentrated than usually required; but once standardized and maintained at constant temperature, volumetric dilutions of the stock solution with carbon dioxide-free water can be made as needed. Barium hydroxide solution is standardized against potassium acid phthalate or benzoic acid, as described for sodium hydroxide.

## PRECIPITATION METHODS

In addition to the use of visual indicators in precipitation methods, end-point detection by electrical methods (potentiometric, conductometric) is applicable in many instances; pH control, change of solvent, back titration of excess precipitant, etc., may be used to approach the conditions required for exact stoichiometry. The methods given here are limited to those involving visual detection of the end point.

### SILVER NITRATE (ARGENTOMETRIC) METHODS

*Primary Standards and Standard Solutions.*—Metallic silver, silver nitrate, potassium chloride, sodium chloride, and potassium thiocyanate are easily obtained in high purity,<sup>14</sup> and can be used as primary standards, including direct preparation of standard solutions. It is often convenient to have a silver nitrate solution which has been standardized against a chloride solution and/or a thiocyanate solution, to facilitate corrections for titration error in analyzing unknowns.

Silver Nitrate ( $\text{AgNO}_3$ , mol. wt. and equiv. wt. = 169.89).—Use analytical reagent grade silver nitrate; if in large crystals, grind to small size. Dry for 1 to 2 hours at 100°C., taking care to exclude dust and other reducing materials. For an exact 0.1 N solution, accurately weigh 16.989 g. of the dried silver nitrate and make up volumetrically to 1 liter.<sup>15</sup> (For an approximate 0.1 N solution, rough weigh 17 g.

<sup>14</sup> See Kolthoff, I. M., and Sarver, W. A., *Volumetric Analysis*, Vol. II, Interscience Publishers, Inc., New York, pp. 251–254, 1947.

<sup>15</sup> If pure metallic silver is available, a direct standard solution of silver nitrate can be prepared by dissolving a known weight of the metal in 1:1 nitric acid; evaporate to expel excess acid, then dilute to known volume. However, for some applications (e.g., the Mohr method for halides), free nitric acid cannot be tolerated.



of the solid and make up to about a liter.) Store the solution in a brown bottle, and protect the stopper and neck from dust. Check the normality of the direct solution, or standardize the approximate solution, against chloride and/or against thiocyanate.

**Potassium Thiocyanate (KSCN, mol. wt. and equiv. wt. = 97.185).**—The pure salt is dried in a desiccator over sulfuric acid; it is not hygroscopic in an atmosphere of relative humidity less than 50%. For preparation of a direct 0.1 *N* solution, weigh 9.718 g. of the pure dry solid, dissolve in water, and make up to 1 liter.

**Potassium Chloride or Sodium Chloride (KCl, mol. wt. and equiv. wt. = 74.557; NaCl, mol. wt. and equiv. wt. = 58.448).**—The analytical reagent grades are satisfactory primary standards for ordinary work. For a liter of exact 0.1 *N* solution take 7.456 g. of KCl or 5.845 g. of NaCl, and make to volume with water.

**Indicators.** **Ferric Alum (for Volhard Method).**—Dissolve 280 g. of ferric ammonium sulfate hydrate in 900 ml. of hot water. Cool, let settle, and pour off (or filter) from any residue, then add 100 ml. of concentrated nitric acid to the solution. Use about 5 ml. of indicator per 100 ml. of titration solution. In the Volhard method the end point is the first red color, due to formation of  $[\text{FeSCN}]^{++}$  after precipitation of  $\text{AgSCN}$  is complete.

**Potassium Chromate (for Mohr Method).**—Prepare a 5% aqueous solution of  $\text{K}_2\text{CrO}_4$ ; use 1 ml. of indicator per 100 ml. final volume of titration solution. In the titration of chloride (or bromide) the end point is the formation of the first detectable red-orange precipitate of  $\text{Ag}_2\text{CrO}_4$  after precipitation of the silver halide is complete.

**Dichlorofluorescein (for Fajans Method for Chloride).**—Prepare a 0.1% solution of dichlorofluorescein in alcohol, or of its sodium salt in water. Use about ten drops per 100 ml. of solution.

**Eosin (for Fajans Method for Bromide, Iodide, Thiocyanate).**—Prepare a 0.5% solution of eosin (tetrabromofluorescein) in alcohol, or of its sodium salt in water.

In the adsorption indicator methods a protective colloid is used to prevent the coagulation of the precipitate. A 2% aqueous solution of dextrin is commonly employed; discard the stock solution if mold formation is apparent.

### PROCEDURES

The procedures given below apply to titrations of primary standards or standard solutions for purposes of standardization or comparison, and to titrations of unknowns from which interfering substances have been removed.

**Titration of Silver Ion with Thiocyanate (Volhard Method).**—The sample solution should be at least 0.3 *N* in acid, usually nitric acid although sulfuric acid is sometimes used. If the solution is not already acidic, add 5 ml. of 6 *M* nitric acid which is free from chloride ion and from oxides of nitrogen (boil, if necessary, to remove oxides of nitrogen), add 5 ml. of ferric alum indicator, and titrate with potassium thiocyanate solution to the first red-orange tinge in the solution. Because silver thiocyanate precipitate adsorbs silver ion from solution, the first indication of the end point may come too early; vigorous shaking during dropwise completion of the titration is required, until a faint but permanent red-orange color is obtained. Run a blank, using the same amount of nitric acid, indicator, and water, and correct the titration volume for the amount of the blank; the blank should be very small.

**Titration of Chloride with Silver Ion. a. Mohr Method.**—The allowable range of pH is about 6.5 to 10; below pH 6.5 the increased solubility of silver chromate

makes the end point come too late; above pH 10, silver hydroxide is also precipitated. If the solution for titration is strongly alkaline, make it just acidic with nitric acid, then neutralize by adding sodium bicarbonate or borax; if the solution is already acidic, neutralize with sodium bicarbonate or borax. If appreciable amounts of ammonium salts are present, the pH should not exceed 7.2. To the solution for titration, adjusted in pH as indicated above, add 1 ml. of potassium chromate indicator for each 100 ml. final volume, and titrate with silver nitrate solution, with good stirring or shaking especially near the end, to the first permanent red-orange tinge. It is advisable to save the samples from the first two titrations. To one sample, add a minute amount of chloride and stir, to transpose the silver chromate and restore the yellow color. These samples are then used for comparison in adjusting the end point in titration of subsequent samples. Observation of the end point is sharpened by making the titration under a yellow light. Run a blank, using about 0.3 g. of chloride-free calcium carbonate (to simulate the precipitate) and the same amount of indicator and same final volume of water. The method is applicable to determination of low concentrations of chloride, as in water analysis. It is also applicable to the determination of bromide, but not to iodide nor thiocyanate. The reverse titration (silver ion titrated by chloride) is generally unsatisfactory on account of the slow transposition of silver chromate to silver chloride near the equivalence point.

b. *Fajans Method.*—The allowable range of pH is 4 to 10, and the chloride concentration should be in the range 0.005 to 0.025 *N*. To the solution for titration add 5 ml. of 2% dextrin solution and ten drops of 0.1% dichlorofluorescein indicator. Titrate, in subdued light, with silver nitrate to the color change from greenish-yellow in the solution to a salmon-pink color on the suspended precipitate. A blank test cannot be made. Titration of silver ion by chloride is also satisfactory, the end point being the disappearance of the salmon-pink color from the suspension. If photochemical action on the silver chloride causes it to turn gray, a satisfactory end point cannot be obtained. The general method is applicable also to the titration of bromide, iodide, and thiocyanate, using eosin indicator; the allowable pH is 2 to 10.

c. *Volhard Method.*—The chloride is precipitated by adding a known amount of silver nitrate, in excess of that required for precipitation of silver chloride; the amount of the excess is determined by back titration with thiocyanate solution. Correct stoichiometry requires a procedure to prevent transposition of silver chloride to the less soluble silver thiocyanate during back titration and/or removal of silver ion adsorbed on the silver chloride precipitate. Use one of the following methods.

(i) *Original Volhard Method.* The solution for titration should be about 0.3 *M* in chloride-free nitric acid. Add a measured volume of standard silver nitrate solution, in excess of the amount to precipitate the chloride as AgCl. Boil to coagulate the precipitate, filter it off (use fritted glass crucible), and wash it well with 1:100 nitric acid. Titrate the filtrate and washings with standard potassium thiocyanate solution, using 5 ml. of ferric alum indicator exactly as described earlier for the Volhard method. From the total amount of silver nitrate added, subtract the amount equivalent to the thiocyanate back titration to get the net amount of silver nitrate required to precipitate the chloride.

(ii) *Caldwell Modification.*<sup>16</sup> The solution for titration should contain about 0.05 to 0.25 g. of alkali chloride in 25 to 50 ml. of water plus 2 to 5 ml. of chloride-

<sup>16</sup> Caldwell, J. R., and Moyer, H. V., *Ind. Eng. Chem., Anal. Ed.*, 7, 38, 1935.

free 6 *M* nitric acid. To the solution add 1 ml. of nitrobenzene for each 0.05 g. of chloride. Add a measured volume of standard silver nitrate solution, in excess of the amount to precipitate the chloride. Stopper the flask and shake vigorously to coagulate the precipitate and coat the particles with nitrobenzene. Add 5 ml. of ferric alum indicator, and titrate the excess silver ion with standard thiocyanate solution to the first faint red-orange tinge. Adequate stirring near the end point is required, but violent shaking should be avoided. Calculate as in (i) above.

The Volhard method is applicable also to the determination of bromide and iodide; in these cases, removal or protection of the silver halide precipitate is unnecessary. In the determination of iodide, ferric alum indicator must not be added until after the precipitation of the silver iodide.

### MERCURIMETRIC METHOD FOR CHLORIDE

Although this method is not a precipitation titration, it is treated here for convenience. The method depends upon the formation of slightly ionized mercury(II) chloride,  $\text{HgCl}_2$ , when a soluble chloride is treated with a highly ionized mercury(II) solution, such as the nitrate or perchlorate. Sodium nitroprusside indicator shows a white turbidity of  $\text{HgFe}(\text{CN})_5\text{NO}$  when mercury(II) is present in excess. A slight end-point error can be evaluated by running a blank containing about the same concentration of mercury(II) chloride as in the sample solution; no correction need be applied if the mercury(II) solution is standardized against chloride of about the same amount as in unknown samples. The method is especially suited to the determination of small amounts of chloride, and to chloride in acid solution. Diphenylcarbazide or diphenylcarbazone indicator<sup>17</sup> requires closer control of conditions than when sodium nitroprusside indicator is used.

**Reagents.**—The mercury(II) solution may be either the nitrate or the perchlorate.

**Mercury(II) Nitrate.**—Dissolve about 17 g. of mercury(II) nitrate hemihydrate (mol. wt. = 333.63; equiv. wt. = 166.82) in 50 ml. of 6 *M* nitric acid and dilute to about 1 liter; standardize against chloride. Alternatively, dissolve about 11 g. of mercury(II) oxide (mol. wt. = 216.61; equiv. wt. = 108.30) in a slight excess of 6 *M* nitric acid and dilute to about 1 liter; standardize against chloride.

**Mercury(II) Perchlorate.**—Dissolve about 11 g. of mercury(II) oxide in a slight excess of 1:1 perchloric acid and dilute to about 1 liter; standardize against chloride.

**Sodium Nitroprusside Indicator.**—Prepare a 10% aqueous solution of sodium nitroprusside,  $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ . Store in a brown bottle; discard if the solution turns green.

**Primary Standard Potassium Chloride or Sodium Chloride.**—See under Silver Nitrate Methods.

**Procedure.**—Cations which form slightly soluble nitroprussides (e.g., cadmium, copper, cobalt, nickel) must be absent. To the chloride solution add nitric acid to make its concentration 0.2 to 0.5 *M*, and two drops of sodium nitroprusside indicator for each 10 ml. of solution. Titrate slowly against a black background to the first faint permanent turbidity. If the mercury(II) solution is to be used for titrations other than chloride, run a blank, using about the same amount of mercury(II) chloride, nitric acid, indicator, and final volume as in the titration; the blank usually amounts to 0.1–0.2 ml. in titrations with 0.1 *N* mercury(II) solution. For titration of small amounts of chloride, use a mercury(II) solution of about 0.02 *N* concentration.

<sup>17</sup> Roberts, I., *Ind. Eng. Chem., Anal. Ed.*, 8, 365, 1936.

The method is also applicable to titration of bromide. Thiocyanate can be determined, using ferric alum indicator and titration to the disappearance of red color. Cyanide can be determined by adding excess standard mercury(II) solution, then back titrating with standard thiocyanate, using ferric alum indicator.

## COMPLEXATION METHODS

In spite of the large number of complex ions that are known, relatively few methods involving complex formation are applicable to titration because of the existence of several complexes between a central metal ion and the ligand (complexing agent). Therefore, the conditions of exact stoichiometry are rarely fulfilled. A notable exception is the reaction of metal ions with ethylenediaminetetraacetic acid (EDTA).

## METHODS INVOLVING CYANIDE

*Titration of Cyanide by Silver Ion (Liebig-Denigès Method).* Standard Silver Nitrate.—Prepare standard silver nitrate solution, as given previously under Precipitation Methods.

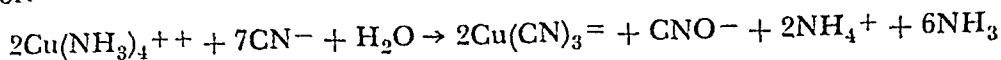
*Procedure.*—(Caution: Cyanides and HCN are violently poisonous.) To the cyanide solution for titration add 0.2 g. of potassium iodide and 5 ml. of 6 M ammonia for each 100 ml. of solution. Titrate with standard silver nitrate, against a black background, to the first permanent white turbidity. For calculation to  $CN^-$ , HCN, or alkali cyanide (KCN, NaCN), the equivalent weight is twice the molecular weight:  $2CN^- + Ag^+ \rightarrow Ag(CN)_2^-$ .

*Titration of Cyanide and Chloride in Same Mixture.*—Titrate the solution containing cyanide and chloride with standard silver nitrate solution, to the first permanent white turbidity, due to the start of the reaction  $Ag(CN)_2^- + Ag^+ \rightarrow 2AgCN$  (ppt.). Then add a measured additional volume of standard silver nitrate, in excess of the amount to precipitate completely  $AgCN$  and  $AgCl$ . Filter off the precipitated silver salts on a fritted glass crucible, and wash the precipitate several times with 1:100 nitric acid. To the filtrate and washings add 5 ml. of ferric alum indicator, and titrate the excess silver ion with standard potassium thiocyanate to the first permanent red-orange tinge. From the amount (in numbers of milliequivalents, if the  $AgNO_3$  and  $KSCN$  are of different normalities) of additional silver nitrate beyond the first turbidity subtract the amount of silver nitrate required to produce the first turbidity and the amount of silver nitrate equivalent to the thiocyanate in the back titration; the difference represents silver nitrate equivalent to chloride.

The method is applicable also to titration of a mixture of cyanide with bromide or with thiocyanate.

*Titration of Metal Ions with Cyanide. Potassium Cyanide Solution.* (KCN, mol. wt. = 65.12; equiv. wt. for complexation = 130.24).—For preparation of approximately 0.1 N solution, dissolve about 13 g. of KCN (Caution! Poison!) and 5 g. of sodium hydroxide in water and dilute to about a liter. Standardize by titrating a measured volume (about 40 ml.) of the KCN solution with standard silver nitrate, using the Liebig-Denigès method given previously. Alternatively, standardize the potassium cyanide solution against pure copper; dissolve an accurately weighed amount of pure copper in 6 M nitric acid, make the solution just alkaline to ammonia, and add 5 ml. of 1:1 ammonia in excess. Titrate the deep-blue copper

solution with the potassium cyanide solution just to the disappearance of the blue color:

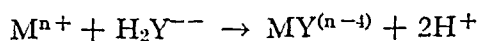


Calculate the copper titer of the potassium cyanide solution (grams or milligrams of copper equivalent to 1.00 ml. of KCN solution).

**Determinations.**—Potassium cyanide solution is most often used in the titrimetric determination of copper and of nickel. Details of procedures are given elsewhere.<sup>18</sup>

## TITRATIONS WITH ETHYLENEDIAMINETETRAACETIC ACID (EDTA)<sup>19</sup>

Ethylenediaminetetraacetic acid (EDTA, commonly represented in equations by  $\text{H}_4\text{Y}$ ), or more often its disodium salt ( $\text{Na}_2\text{H}_2\text{Y}$ ), finds wide application as an analytical reagent in forming complexes with most cations except the alkalis. It can be used to mask the reactions of certain cations to prevent their interference with other reactions; it enhances the color of colored cations, and thus it can be used in spectrophotometric determinations; and it is used for the complexometric titration of many cations. It is apparently unique among complexing agents in forming 1:1 complexes with cations regardless of their valence:



(The general definition of equivalency previously given will still apply to EDTA, but it may be more convenient to express its concentration on a molar basis, or as a titer for a given element.) Titrations with EDTA may be direct, or back titration of excess reagent, or displacement of one cation by another.

**Indicators.**—A wide variety of end-point methods can be applied to titrations with EDTA; use of metal indicators is the most common.<sup>20,21</sup> The metal indicators are compounds which react with metal ions to form highly colored complexes, but which have a different (or no) color in the absence (i.e., very low concentration) of the metal ion. Upon titration with EDTA, the metal-indicator complex transposes to the metal-EDTA complex:  $\text{M-Ind} + \text{Y} \rightarrow \text{M-Y} + \text{Ind}$ . For a direct titration the metal-indicator complex must be less stable than the metal-EDTA complex. Applications of EDTA titrations are so varied and the indicators so numerous that only very few can be mentioned here; for a complete treatment, see Welcher.<sup>19</sup>

**Eriochrome Black T.**—This compound, sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-4-sulfonate, known by many trivial names, has been widely used as an indicator for many metal ions, which form red complexes in alkaline solution; the free dye is blue in alkaline solution. In direct titration methods, the color change is from the red color of the metal-indicator complex to the blue color of the dye as the more stable metal-EDTA complex is formed. This indicator is also used in back titration and in displacement methods.

<sup>18</sup> Furman, N. Howell, *Standard Methods of Chemical Analysis*, 6th Ed., Vol. I, D. Van Nostrand Co., Inc., Princeton, N. J., 1962.

<sup>19</sup> Welcher, F. J., *The Analytical Uses of Ethylenediaminetetraacetic Acid*, D. Van Nostrand Co., Inc., Princeton, N. J., 1958.

<sup>20</sup> Barnard, A. J., Jr., Broad, W. C., and Flaschka, H., *Chemist-Analyst*, 45, 86, 111, 1956; 46, 18, 46, 1957.

<sup>21</sup> Reilley, C. N., and Schmidt, R. W., *Anal. Chem.*, 31, 387, 1959.

0.07 g. of the solid indicator–potassium chloride–charcoal mixture), and 5 ml. of 1 M sodium hydroxide containing 1 g. of sodium cyanide per 100 ml. Titrate with the EDTA solution to the color change from yellow-green to brown. Vigorous stirring throughout the titration is necessary. Do not titrate under strong illumination or under a fluorescent lamp.

**Applications.**—Titrations with EDTA are used extensively for the determination of calcium and/or magnesium hardness in water analysis; procedural details are given elsewhere.<sup>23</sup> For applications in the titrimetric determination of many other cations, see the treatise by Welcher<sup>24</sup> and the literature references given therein.

## OXIDATION-REDUCTION (REDOX) METHODS<sup>25</sup>

Oxidation-reduction methods depend upon the transfer of (one or more) electrons from the reducing agent to the oxidizing agent. The substance titrated must all be in a reduced form for titration by an oxidant, or all in an oxidized form for titration by a reductant. Therefore, a preliminary oxidation or reduction may be required prior to titration; for preliminary redox methods, see Ayres<sup>26</sup> or Laitinen.<sup>27</sup>

**Indicators.**<sup>28</sup>—A few oxidants, notably potassium permanganate and iodine, can act as their own indicators. Certain organic compounds can undergo oxidation or reduction, accompanied by a change of color which occurs at a definite potential. For a given titration, a redox indicator should be selected which has a redox potential that coincides with, or is very close to, the equivalence point potential of the titration system; some latitude of choice is permissible because the potential of most redox titration systems changes very rapidly around the equivalence point. The reaction of most redox indicators is reversible; a few, for example, methyl red, methyl orange, and naphthol blue black, are irreversibly oxidized and decolorized by strong oxidants. Potentiometric detection of the end point in redox titrations is often used, but this method is beyond the scope of this treatment. Table 12-3 lists several redox indicators, their color characteristics, and their transition potentials.

Diphenylaminesulfonate (barium or sodium salt) and 1,10-phenanthroline-ferrous complex ("ferroin") are used frequently in titrations with potassium dichromate and cerium(IV) solutions.

**Diphenylaminesulfonate Indicator.**—Prepare a 0.2% aqueous solution of barium or sodium diphenylaminesulfonate. Use five drops of indicator per 100 ml. of solution. The color of the oxidized indicator is purple.

**"Ferroin" Indicator.**—Prepare a 0.025 M aqueous solution of 1,10-phenanthroline ferrous perchlorate (mol. wt. 795), or 1,10-phenanthroline ferrous sulfate (mol. wt.

<sup>23</sup> Furman, N. Howell, *Standard Methods of Chemical Analysis*, 6th Ed., Vol. I, p. 270, D. Van Nostrand Co., Inc., Princeton, N. J., 1962.

<sup>24</sup> Welcher, F. J., *The Analytical Uses of Ethylenediaminetetraacetic Acid*, D. Van Nostrand Co., Inc., Princeton, N. J., 1958.

<sup>25</sup> For a comprehensive treatment, see Kolthoff, I. M., and Belcher, R., *Volumetric Analysis*, Vol. III, Interscience Publishers, Inc., New York, 1957.

<sup>26</sup> Ayres, G. H., *Quantitative Chemical Analysis*, Chap. 23, Harper and Brothers, New York, 1958.

<sup>27</sup> Laitinen, H. A., *Chemical Analysis*, Chap. 18, McGraw-Hill Book Co., Inc., New York, 1960.

<sup>28</sup> Kolthoff, I. M., and Stenger, V. A., *Volumetric Analysis*, Vol. I, Interscience Publishers, Inc., New York, pp. 105–141, 1942.

**Murexide.**—This compound, the ammonium salt of purpuric acid, has been used especially in the titration of calcium (red complex at pH about 10), cobalt, nickel, and copper (yellow complexes); the dye itself is violet to blue in alkaline solution.

**Calcein.**—This is the trivial name for fluoresceiminodiacetic acid, introduced by Diehl and Ellingboe<sup>22</sup> for use in the titration of calcium ion with EDTA. At pH above 12, the calcium complex is yellow-green and the indicator is brown. Calcein also forms complexes with barium and strontium, but not with magnesium.

**Reagents. Standard Solution of Disodium-EDTA.**—Disodium ethylenediaminetetraacetate dihydrate (mol. wt. 372.2) is available in primary standard quality; hence a standard solution can be made by the direct method. Solutions for various uses will vary in concentration from about 0.1 to 0.01 *M*. For use in determining hardness in water, the solutions are usually made so as to have a simple integral titer of calcium or of calcium carbonate, e.g., 1.00 mg. of calcium carbonate per ml. of EDTA. Dissolve about 5 g. of disodium-EDTA dihydrate in about a liter of water; standardize against calcium as given below.

**pH 10 Buffer.**—Dissolve 68 g. of ammonium chloride in 200 ml. of water; add 570 ml. of concentrated ammonia, and water to make a liter.

**Standard Calcium Solution.**—Dissolve 1.000 g. of pure calcium carbonate in the least amount of dilute hydrochloric acid. Make the solution barely alkaline with ammonia, and dilute with water to exactly 1 liter; 1.00 ml. equals 1.00 mg. calcium carbonate or 0.400 mg. calcium.

**Eriochrome Black T Indicator.**—Dissolve 0.5 g. of the dye and 5 g. of hydroxylamine hydrochloride in 100 ml. of alcohol.

**Murexide Indicator.**—Prepare a fresh saturated aqueous solution (stable for 1 or 2 days). Alternatively, mix the solid indicator with sodium chloride in a 1:100 ratio, and grind intimately.

**Calcein Indicator.**—Dissolve 2 g. of indicator in 25 ml. of 1 *N* sodium hydroxide, and dilute to 100 ml. Alternatively, grind 1 g. of indicator with 100 g. of potassium chloride, or 1 g. of indicator with 10 g. of charcoal and 100 g. of potassium chloride.

**Standardization of EDTA Solution. Using Eriochrome Black T.**—Transfer 25.0 ml. (pipet) of the standard calcium solution to an Erlenmeyer flask, add about 25 ml. of distilled water, 5 ml. of pH 10 buffer solution, two drops of 1% magnesium chloride solution, and five drops of eriochrome black T indicator. Titrate with the EDTA solution to the color change from wine-red to blue; no trace of purple color remains at the correct end point. Run a blank with water, buffer, magnesium chloride, and indicator in the same amounts as in the titration, and subtract the amount of the blank. (If the EDTA solution is to be used only for titration of calcium in the absence of magnesium, add 0.1 g. of  $MgCl_2 \cdot 6H_2O$  to the EDTA solution before standardizing; the magnesium ion provides the indicator action, and no blank correction is necessary.)

**Using Murexide.**—Transfer 25.0 ml. (pipet) of the standard calcium solution to an Erlenmeyer flask, add about 25 ml. of distilled water, 1 ml. of 6 *M* sodium hydroxide, and about 0.2 g. of murexide-sodium chloride indicator mixture (or five drops of fresh saturated solution). Titrate with the EDTA solution to the color change from pink to blue-violet.

**Using Calcein.**—To 25.0 ml. (pipet) of the standard calcium solution add about 75 ml. of distilled water, one or two drops of calcein indicator solution (or about

<sup>22</sup> Diehl, H., and Ellingboe, J. L., *Anal. Chem.*, 28, 882, 1956.

0.07 g. of the solid indicator—potassium chloride—charcoal mixture), and 5 ml. of 1 M sodium hydroxide containing 1 g. of sodium cyanide per 100 ml. Titrate with the EDTA solution to the color change from yellow-green to brown. Vigorous stirring throughout the titration is necessary. Do not titrate under strong illumination or under a fluorescent lamp.

*Applications.*—Titrations with EDTA are used extensively for the determination of calcium and/or magnesium hardness in water analysis; procedural details are given elsewhere.<sup>23</sup> For applications in the titrimetric determination of many other cations, see the treatise by Welcher<sup>24</sup> and the literature references given therein.

## OXIDATION-REDUCTION (REDOX) METHODS<sup>25</sup>

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*Indicators.*<sup>28</sup>—A few oxidants, notably potassium permanganate and iodine, can act as their own indicators. Certain organic compounds can undergo oxidation or reduction, accompanied by a change of color which occurs at a definite potential. For a given titration, a redox indicator should be selected which has a redox potential that coincides with, or is very close to, the equivalence point potential of the titration system; some latitude of choice is permissible because the potential of most redox titration systems changes very rapidly around the equivalence point. The reaction of most redox indicators is reversible; a few, for example, methyl red, methyl orange, and naphthol blue black, are irreversibly oxidized and decolorized by strong oxidants. Potentiometric detection of the end point in redox titrations is often used, but this method is beyond the scope of this treatment. Table 12-3 lists several redox indicators, their color characteristics, and their transition potentials.

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*Diphenylaminesulfonate Indicator.*—Prepare a 0.2% aqueous solution of barium or sodium diphenylaminesulfonate. Use five drops of indicator per 100 ml. of solution. The color of the oxidized indicator is purple.

*"Ferroin" Indicator.*—Prepare a 0.025 M aqueous solution of 1,10-phenanthroline ferrous perchlorate (mol. wt. 795), or 1,10-phenanthroline ferrous sulfate (mol. wt.

<sup>23</sup> Furman, N. Howell, *Standard Methods of Chemical Analysis*, 6th Ed., Vol. I, p. 270, D. Van Nostrand Co., Inc., Princeton, N. J., 1962.

<sup>24</sup> Welcher, F. J., *The Analytical Uses of Ethylenediaminetetraacetic Acid*, D. Van Nostrand Co., Inc., Princeton, N. J., 1958.

<sup>25</sup> For a comprehensive treatment, see Kolthoff, I. M., and Belcher, R., *Volumetric Analysis*, Vol. III, Interscience Publishers, Inc., New York, 1957.

<sup>26</sup> Ayres, G. H., *Quantitative Chemical Analysis*, Chap. 23, Harper and Brothers, New York, 1958.

<sup>27</sup> Laitinen, H. A., *Chemical Analysis*, Chap. 18, McGraw-Hill Book Co., Inc., New York, 1960.

<sup>28</sup> Kolthoff, I. M., and Stenger, V. A., *Volumetric Analysis*, Vol. I, Interscience Publishers, Inc., New York, pp. 105-141, 1942.



filter through fritted glass.<sup>31</sup> Alternatively, make up a large amount (e.g., carboy) of solution at room temperature and store in the dark for several weeks or months; siphon off the solution and filter through a glass frit in preparation for standardization. Store in a dark bottle. A stock solution should be restandardized from time to time; if any manganese dioxide has formed, filter before restandardizing. Preparation of a dilute standard solution by volumetric dilution of a more concentrated one with ordinary distilled water should not be practiced, on account of the presence of reducing substances in the water.

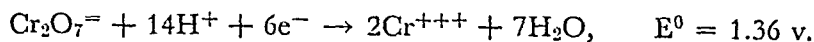
**Standardization.**—Primary standard sodium oxalate and arsenic(III) oxide are available from National Bureau of Standards and from chemical supply firms. Iron wire, ferrous ammonium sulfate hexahydrate, and oxalic acid dihydrate find some use as secondary standards.

**Against Sodium Oxalate** ( $\text{Na}_2\text{C}_2\text{O}_4$ , mol. wt. = 134.01; equiv. wt. = 67.00).—This is the best primary standard for permanganate. Dry the solid at 105°C. Pour 50 ml. of concentrated sulfuric acid slowly and with good stirring into 950 ml. of distilled water; boil the solution for 10 to 15 minutes, then cool to room temperature. For standardization of 0.1 *N* permanganate, accurately weigh about 0.3 g. of the dry sodium oxalate and dissolve it in 250 ml. of the dilute sulfuric acid. Add about 90% of the expected volume of permanganate solution, with gentle stirring. Let stand until the permanganate color disappears (30 to 60 sec.) then heat the solution to about 60°C. and complete the titration to a faint pink color that persists for 30 seconds. The last milliliter or so of the permanganate should be added dropwise, allowing each drop to be decolorized before adding the next. Determine the blank using 250 ml. of the dilute sulfuric acid at 60°C. The blank usually amounts to 0.05 ml. or less.

**Against Arsenic(III) Oxide** ( $\text{As}_2\text{O}_3$ , mol. wt. = 197.82; equiv. wt. = 49.455).—Dry the primary standard at 105°C. To an accurately weighed 0.2-g. sample of dry standard add 10 ml. of 5 *M* sodium hydroxide solution; stir until the solid is completely dissolved, add about 100 ml. of distilled water, 10 ml. of concentrated hydrochloric acid, and one drop of 0.025 *M* potassium iodate or potassium iodide (catalyst).<sup>32</sup> Titrate with potassium permanganate, dropwise near the end, to the first pink color permanent for 30 seconds. Run a blank, using the same amounts of alkali, water, acid, and catalyst as in the titration.

## POTASSIUM DICHROMATE METHODS

As a titrimetric oxidant, the half-reaction equation for dichromate is:



Potassium dichromate is a slightly weaker oxidizing agent than permanganate, which is advantageous for titrations in hydrochloric acid solution; it has the further advantages of being a primary standard, and of great stability of the solution. Because of the color of the reduced form ( $\text{Cr}^{+++}$ , green), a redox indicator is required.

**Preparation of Standard Solution.**—Primary standard potassium dichromate is available from National Bureau of Standards. For ordinary use, analytical reagent

<sup>31</sup> Manganese dioxide is easily removed from the glass frit, after use, by treatment with hydrogen peroxide containing a small amount of nitric acid; wash the frit well before reuse.

<sup>32</sup> Alternatively, 2 drops of 0.01 *M* solution of osmium tetroxide solution can be used as a catalyst.

TABLE 12-3. REDOX INDICATORS <sup>30</sup>

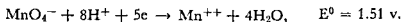
Indicator	Color		E <sup>0</sup> , v.
	Reduced	Oxidized	
Indigo monosulfonate.. . . . .	Colorless	Blue	0.26
Phenosafranine . . . . .	Colorless	Blue	0.28
Methylene blue . . . . .	Colorless	Green-blue	0.36
1-Naphthol-2-sulfonic acid indophenol . . . . .	Colorless	Red	0.54
3,3'-Dimethylnaphthadine . . . . .	Colorless	Red-purple	0.71
Diphenylamine . . . . .	Colorless	Violet	0.76
3,3'-Dimethylnaphthadine sulfonate.. . . .	Colorless	Red-purple	0.80
Diphenylamine sulfonic acid.. . . .	Colorless	Violet	0.84
N,N'-Tetramethylbenzidine-3-sulfonic acid.. . . .	Colorless	Yellow	0.88
Ferrous 2,2'-bipyridine sulfate.. . . .	Red	Blue	0.97
Erioglaucine A. . . . .	Red	Green	1.00
Ferrous 5-methyl-1,10-phenanthroline sulfonate.. . . .	Red	Blue	1.02
Ferrous 1,10-phenanthroline(ferroin) . . . . .	Red	Blue	1.06
<i>p</i> -Nitrodiphenylamine.. . . .	Colorless	Violet	1.06
Ferrous 5-nitro-1,10-phenanthroline(nitroferroin).. . . .	Red	Blue	1.25
Ruthenium tridipyridine dichloride . . . . .	Colorless	Yellow	1.33

<sup>30</sup> Taken from Ayres, G. H., *Quantitative Chemical Analysis*, Harper and Brothers, New York, p. 417, 1958. Used by permission of the publisher.

692).<sup>29</sup> The analyst will find that the reduced form is an intense red, whereas the oxidized form is a very pale blue.

### POTASSIUM PERMANGANATE METHODS

Although potassium permanganate can undergo several different reductions, it is most commonly used in acid solution under conditions that give reduction to manganese(II):



In neutral solution permanganate slowly decomposes, and it is also reduced by dust, organic matter, etc., in the water; the manganese dioxide formed by these reactions catalyzes the further decomposition of the permanganate. Permanganate solutions must be prepared empirically and then standardized.

**Preparation of Solution.**—For each liter of 0.1 N solution to be prepared, use about 3.2 g. of potassium permanganate. Dissolve the desired amount of the salt in water, and boil the solution for one-half hour; allow to stand for 24 hours, then

<sup>29</sup> Obtainable as solids, or prepared in solution, from G. Frederick Smith Chemical Co., 867 McKinley Ave., Columbus 22, Ohio.

filter through fritted glass.<sup>31</sup> Alternatively, make up a large amount (e.g., carboy) of solution at room temperature and store in the dark for several weeks or months; siphon off the solution and filter through a glass frit in preparation for standardization. Store in a dark bottle. A stock solution should be restandardized from time to time; if any manganese dioxide has formed, filter before restandardizing. Preparation of a dilute standard solution by volumetric dilution of a more concentrated one with ordinary distilled water should not be practiced, on account of the presence of reducing substances in the water.

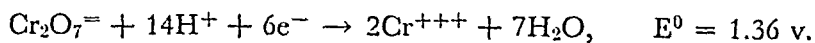
**Standardization.**—Primary standard sodium oxalate and arsenic(III) oxide are available from National Bureau of Standards and from chemical supply firms. Iron wire, ferrous ammonium sulfate hexahydrate, and oxalic acid dihydrate find some use as secondary standards.

**Against Sodium Oxalate** ( $\text{Na}_2\text{C}_2\text{O}_4$ , mol. wt. = 134.01; equiv. wt. = 67.00).—This is the best primary standard for permanganate. Dry the solid at 105°C. Pour 50 ml. of concentrated sulfuric acid slowly and with good stirring into 950 ml. of distilled water; boil the solution for 10 to 15 minutes, then cool to room temperature. For standardization of 0.1 *N* permanganate, accurately weigh about 0.3 g. of the dry sodium oxalate and dissolve it in 250 ml. of the dilute sulfuric acid. Add about 90% of the expected volume of permanganate solution, with gentle stirring. Let stand until the permanganate color disappears (30 to 60 sec.) then heat the solution to about 60°C. and complete the titration to a faint pink color that persists for 30 seconds. The last milliliter or so of the permanganate should be added dropwise, allowing each drop to be decolorized before adding the next. Determine the blank using 250 ml. of the dilute sulfuric acid at 60°C. The blank usually amounts to 0.05 ml. or less.

**Against Arsenic(III) Oxide** ( $\text{As}_2\text{O}_3$ , mol. wt. = 197.82; equiv. wt. = 49.455).—Dry the primary standard at 105°C. To an accurately weighed 0.2-g. sample of dry standard add 10 ml. of 5 *M* sodium hydroxide solution; stir until the solid is completely dissolved, add about 100 ml. of distilled water, 10 ml. of concentrated hydrochloric acid, and one drop of 0.025 *M* potassium iodate or potassium iodide (catalyst).<sup>32</sup> Titrate with potassium permanganate, dropwise near the end, to the first pink color permanent for 30 seconds. Run a blank, using the same amounts of alkali, water, acid, and catalyst as in the titration.

## POTASSIUM DICHROMATE METHODS

As a titrimetric oxidant, the half-reaction equation for dichromate is:



Potassium dichromate is a slightly weaker oxidizing agent than permanganate, which is advantageous for titrations in hydrochloric acid solution; it has the further advantages of being a primary standard, and of great stability of the solution. Because of the color of the reduced form ( $\text{Cr}^{+++}$ , green), a redox indicator is required.

**Preparation of Standard Solution.**—Primary standard potassium dichromate is available from National Bureau of Standards. For ordinary use, analytical reagent

<sup>31</sup> Manganese dioxide is easily removed from the glass frit, after use, by treatment with hydrogen peroxide containing a small amount of nitric acid; wash the frit well before reuse.

<sup>32</sup> Alternatively, 2 drops of 0.01 *M* solution of osmium tetroxide solution can be used as a catalyst.

grade potassium dichromate in fine crystals is satisfactory. If the purity is in doubt, recrystallize three times from water. The solid should be dried at 150° to 200°C. For a liter of exactly 0.1 *N* solution, weigh 4.904 g. of pure standard ( $K_2Cr_2O_7$ , mol. wt. = 294.22; equiv. wt. = 49.035), dissolve in and make up to volume with distilled water. If desired, the normality of an empirically prepared solution may be determined by standardization against arsenic(III) oxide,<sup>33</sup> or against a like material (e.g., NBS iron ore if the dichromate is to be used for the determination of iron). In the titration of iron(II), use five drops of diphenylaminesulfonate indicator, and titrate to the color change from green ( $Cr^{++}$ ) to purple of the oxidized indicator.

### CERIUM(IV) METHODS<sup>34</sup>

The simple half-reaction  $Ce^{4+} + e \rightleftharpoons Ce^{3+}$  does not represent the true situation in solution on account of complex formation of cerium(IV), and to some extent of cerium(III), with various anions as well as with water. The redox potential varies from about 1.3 v. to about 1.9 v., depending upon the anion present and the acid concentration. Solutions of cerium(III) are colorless; although the yellow-orange color of cerium(IV) can be used as a self-indicator, titrations with cerium(IV) are generally made with an indicator, such as ferroin or nitroferroin. Only one reduction product is possible. Cerium(IV) can be used with solutions up to 3 *M* in hydrochloric acid; acidified sulfate solutions can withstand prolonged boiling without loss of oxidizing capacity.

**Preparation of Solution.**—Ammonium hexanitratocerate(IV) is available in primary standard purity, and can be used for preparation of a direct standard solution. If nitrate ion cannot be tolerated in its intended use, it can be removed by fuming down with sulfuric acid. Empirical solutions can be made by dissolving cerium(IV) oxide or sulfate, or ammonium trisulfatocerate(IV) in sulfuric acid sufficient to give a final solution about 0.5 to 1 *N* in sulfuric acid.

**Direct Standard Solution.**—Dry the primary standard ammonium hexanitratocerate(IV) at 85°C. for 4 to 6 hours. For a liter of exact 0.1 *N* solution, weigh out 54.83 g. of the dry  $(NH_4)_2Ce(NO_3)_6$  (mol. wt. and equiv. wt. = 548.26), add 55 ml. of concentrated sulfuric acid, and stir for 2 minutes. Add 100 ml. of distilled water gradually over several minutes, without stirring. Repeat the addition of 100 ml. of water, with good stirring, several more times. When dissolution is complete, transfer to a 1-liter flask and dilute to volume.

**Empirical Solution.**—For a liter of 0.1 *N* solution, use about 17 g. of  $CeO_2$ , or 33 g. of  $Ce(SO_4)_2$ , or 50 g. of  $(NH_4)_2Ce(SO_4)_3 \cdot 2H_2O$ . Dissolve the solid in sulfuric acid as described above for the direct standard solution, and dilute to about a liter. Standardize by one of the methods given below.

**Standardization. Preparation of Catalyst.** *a. Iodine Monochloride.*<sup>35</sup>—To 20 ml. of 0.025 *M* potassium iodate add 25 ml. of 0.04 *M* potassium iodide and 40 ml. of concentrated hydrochloric acid. Add 5 to 10 ml. of carbon tetrachloride, and either more iodate or more iodide (dropwise) as needed until the carbon tetrachloride, after good shaking and settling, has only a barely perceptible pink color of free iodine. The aqueous solution is about 0.017 *M* in iodine monochloride,  $ICl$ . *b. Osmium Tetroxide.* Prepare a 0.25% (about 0.01 *M*) solution of osmium tetroxide (osmic acid) in 0.1 *M* sulfuric acid.

<sup>33</sup> Willard, H. H., and Young, P., *Ind. Eng. Chem., Anal. Ed.*, **7**, 57, 1935.

<sup>34</sup> For an excellent survey of cerium(IV) oxidimetry, see Laitinen, H. A., *op. cit.*

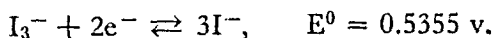
<sup>35</sup> Willard, H. H., and Young, P., *J. Am. Chem. Soc.*, **50**, 1322, 1928; **55**, 3260, 1933.

**Standardization Against Sodium Oxalate** ( $\text{Na}_2\text{C}_2\text{O}_4$ , mol. wt. = 134.01; equiv. wt. = 67.00).—Dissolve an accurately weighed sample (about 0.25 g.) of dry primary standard sodium oxalate in 75 ml. of water. Add 20 ml. of concentrated hydrochloric acid and 1.5 ml. of 0.017 *M* iodine monochloride. Heat the solution to from 45 to 50°C. (temperature limits are important), add one or two drops of 0.025 *M* ferroin indicator and titrate with the cerium(IV) solution to the color change from red to pale blue or colorless, with no return of the pink color within 1 minute. Titration without a catalyst can be made as follows: dissolve the sodium oxalate in 200 ml. of 1:10 (by volume) hydrochloric acid. Heat the solution to 70°C. and titrate to the first faint permanent yellow color of excess cerium(IV). Run a blank on 200 ml. of water containing 1 ml. of concentrated sulfuric acid; heat to 70°C. and titrate to the same color. The blank is usually about 0.05 ml. of 0.1 *N* solution.

**Standardization Against Arsenic(III) Oxide** ( $\text{As}_2\text{O}_3$ , mol. wt. = 197.82; equiv. wt. = 49.455).—Dissolve the dry, weighed primary standard (about 0.2 g.) in 10 ml. of 1 *N* sodium hydroxide, add 50 ml. of 1 *N* sulfuric acid, three drops of osmium tetroxide catalyst, and one or two drops of ferroin indicator. Titrate, slowly near the end, until the red color is discharged.

### IODINE METHODS

The half-reaction  $\text{I}_2 + 2e^- \rightleftharpoons 2\text{I}^-$ , or more correctly



can be used analytically in either direction. Strong reductants can be titrated directly with iodine solution (iodimetry), and strong oxidants can be determined indirectly by oxidation of iodide to free iodine which is titrated with sodium thiosulfate solution (iodometry). The principal sources of error are air oxidation of iodide (which is catalyzed by many substances), and loss of iodine by volatilization.

**Indicators.**—Starch imparts a deep-blue color to iodine solution even at very low concentration ( $10^{-5}$  *N*); however, no color develops in aqueous solutions near the boiling point, or in solutions containing a high concentration (e.g., 50% or more) of ethanol, and starch cannot be used in strongly acidic solutions. In indirect iodine methods the starch indicator should not be added until most of the iodine has been reduced. Starch indicator should be freshly prepared, or stabilized by addition of a preservative such as mercuric iodide or formamide. A water-immiscible organic liquid, such as carbon tetrachloride or chloroform, can often be used advantageously as indicator; a distinct pink color is imparted to the organic phase by a very low concentration of iodine.

**Preparation of Starch Indicator.**—Mix 2 g. of soluble starch with cold water to form a thin, smooth paste. Pour the paste into a liter of boiling water, and boil for a few minutes if necessary to clarify the solution. To the hot solution add a few milligrams of mercuric iodide as a preservative. The solution is stable for long periods, but it should be discarded if it gives with iodine a violet or red color instead of the characteristic deep-blue color.

**Iodine Solution.**—Although a direct standard solution can be prepared from re-sublimed iodine, the method is inconvenient on account of the technique required in weighing and transferring without loss of iodine by volatilization. It is customary to prepare an approximate solution which is then standardized.

**Preparation of 0.1 N Solution.**—Weigh roughly 13 g. of analytical reagent re-sublimed iodine (equiv. wt. = 126.91) and 40 g. of potassium iodide (free from iodate) and transfer to a mortar. Grind the solids under about 50 ml. of distilled water, pour off the solution into a bottle, and repeat the operation until the solids are all dissolved. Dilute to about a liter, and mix thoroughly. Store in a dark bottle, preferably of resistance glass if long storage is anticipated. It is advisable to let the solution stand for 24 hours or so, with occasional shaking, to ensure complete dissolution of the iodine before standardization.

**Standardization Against Arsenic(III) Oxide ( $As_2O_3$ , mol. wt. = 197.82; equiv. wt. = 49.455).**—Primary standard arsenic(III) oxide, available commercially or from the National Bureau of Standards, is the best standard for iodine solution. Dry the solid at 105°C. Accurately weigh about 0.2 g. of the dry standard into an Erlenmeyer flask; dissolve the solid in 10 ml. of 1 N sodium hydroxide then add 10 to 12 ml. of 1 N sulfuric acid. Dissolve 1 g. of sodium bicarbonate in about 50 ml. of water, and slowly add the bicarbonate solution to the arsenite solution. Add 5 ml. of starch indicator solution, and titrate with the iodine solution to the appearance of the first permanent blue color. A fading end point is due to insufficient bicarbonate; in that event, add more bicarbonate and complete the titration. As an alternative to the use of separate weighed samples of primary standard, measured aliquots of a standard arsenite solution, prepared from primary standard  $As_2O_3$ , can be titrated, in solution buffered with sodium bicarbonate.

**Thiosulfate Solution.**—Pure sodium thiosulfate pentahydrate can be prepared by several recrystallizations from water, followed by drying in air and then over deliquescent calcium chloride hexahydrate. The pure hydrate of sodium thiosulfate is stable over a wide range of relative humidity. Although preparation of a direct standard solution is possible, this would require availability of a large quantity of the pure material. The solution is therefore usually prepared empirically and then standardized. Often it is convenient to have iodine and thiosulfate (or arsenite) solution that have been standardized independently, and the standardizations checked by making a direct comparison titration of the iodine solution by the thiosulfate (or arsenite) solution.

**Preparation of 0.1 N Solution.**—In a large flask, boil about a liter of distilled water for several minutes;<sup>36</sup> stopper the flask and cool the water to room temperature. Dissolve about 25 g. of  $Na_2S_2O_3 \cdot 5H_2O$  (mol. wt. and equiv. wt. = 248.21) in the water, add 1 g. of sodium carbonate, and mix thoroughly.

**Standardization.**—Several different substances are suitable primary standards;<sup>37</sup> iodine, potassium iodate, potassium bromate, potassium hexacyanoferrate(II), potassium dichromate, metallic copper, copper sulfate hexahydrate, etc. The choice may be one of convenience or availability, or may be based on the determination for which the thiosulfate is to be used.

**Against Potassium Iodate ( $KIO_3$ , mol. wt. = 214.01; equiv. wt. = 35.67).**—Analytical reagent potassium iodate is a satisfactory standard; dry it at 160° to 180°C. Transfer the accurately weighed sample, about 0.15 g., to an Erlenmeyer flask; dissolve the solid in about 50 ml. of recently boiled and cooled distilled water. Add

<sup>36</sup> Boiling the water serves to (1) remove dissolved oxygen to decrease the oxygen error; (2) remove carbon dioxide, which causes slow disproportionation of the thiosulfate; (3) destroy microorganisms that decompose thiosulfate. Addition of a small amount of alkali (sodium carbonate) also retards bacterial action.

<sup>37</sup> Kolthoff, I. M., and Belcher, R., *Volumetric Analysis*, Vol. III, Interscience Publishers, Inc., New York, pp. 234-243, 1957.

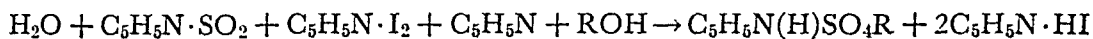
4 g. of potassium iodide, and when it has dissolved add a solution of 1 ml. of concentrated hydrochloric acid in 15 ml. of water. Titrate the liberated iodine at once with the thiosulfate solution until the yellow color is almost discharged, then add 5 ml. of starch indicator solution and complete the titration just to the disappearance of blue color. Run a blank, using the same amount of potassium iodide, hydrochloric acid, water, and indicator.

*Against Metallic Copper* (Cu, at. wt. and equiv. wt. = 63.54).—Clean the superficial corrosion from electrolytic copper foil by short treatment with dilute nitric acid; wash well, and dry thoroughly. Accurately weigh samples of about 0.25 g. Dissolve the metal in dilute nitric acid, and boil down to incipient crystallization. Take up in about 20 ml. of water, carefully add dilute ammonia until present in slight excess, then acidify with acetic acid. Dilute to about 100 ml., add 4 g. of potassium iodide, and titrate the liberated iodine with thiosulfate until the yellow color is almost discharged. Add 2 g. of potassium thiocyanate and 5 ml. of starch indicator, and complete the titration dropwise to disappearance of the blue color.

## DETERMINATION OF WATER BY KARL FISCHER

### METHOD <sup>38, 39, 40</sup>

The direct determination of water by titration with Karl Fischer reagent (KFR), which contains iodine, sulfur dioxide, pyridine, and methanol, finds wide use. The overall reaction can be represented as



For further details of the use of this reagent, see Chapter 21 on The Determination of Water.

*Preparation of Karl Fischer Reagent.*—The reagent generally favored contains iodine, sulfur dioxide, and pyridine in a mole ratio 1:3:10, diluted with methanol (or with methyl "Cellosolve") so that 1 ml. of reagent solution reacts with 3 to 4 mg. of water. Preparation according to Smith, Bryant, and Mitchell <sup>41</sup> is as follows: To a dry 1-liter glass-stoppered bottle transfer 84.7 g. (0.33 mole) of iodine and 269 g. (3.3 moles) of dry pyridine (less than 0.1% water). Shake to dissolve the iodine, then add 667 ml. of anhydrous methanol (less than 0.1% water). Several days before the reagent is needed, cool the stock solution in an ice bath. Collect 64 g. (44.5 ml., 1 mole) of anhydrous liquid sulfur dioxide in a cold trap immersed in solid carbon dioxide and protected from atmospheric moisture. Add the liquid sulfur dioxide slowly to the cold stock solution, and mix by shaking. Stopper the mixture, let it come to room temperature, and allow it to stand a few days before using. The reagent is best used in an all-glass automatic buret and gravity-fill or vacuum-fill reservoir protected with drying tubes. Closed titration systems provided with magnetic stirring are often used, although glass-stoppered volumetric flasks are satisfactory for rapid titration with visual end-point detection.

Because of side reactions, the KFR decreases in strength with age. Most of the

<sup>38</sup> Mitchell, J., Jr., and Smith, D. M., *Aquametry*, Interscience Publishers, Inc., New York, 1948.

<sup>39</sup> Kolthoff, I. M., and Belcher, R., *Volumetric Analysis*, Vol. III, Chap. IX, Interscience Publishers, Inc., New York, 1957.

<sup>40</sup> Mitchell, J., Jr., in *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving, Ed., Part II, Vol. 1, Interscience Publishers, Inc., New York, pp. 82-95, 1961.

<sup>41</sup> Smith, D. M., Bryant, W. M. D., and Mitchell, J., Jr., *J. Am. Chem. Soc.*, **61**, 2407, 1939.

change occurs in the first 2 or 3 days, and after a week the strength changes about 1% per day. A freshly prepared solution should be allowed to stand for at least 24 hours (preferably a few days) before being standardized, and the reagent should be restandardized once or twice each day it is used. A reagent containing all components except sulfur dioxide is more stable and less hygroscopic than the complete reagent; sulfur dioxide is added to the stock solution a few days before the reagent is needed.

**Standardization. Against Water-Methanol Solution.**—Accurately weigh about 15 g. of distilled water into a dry 1-liter volumetric flask, dilute to the mark with anhydrous methanol, and mix thoroughly. Glass-stoppered 100-ml. volumetric flasks stored in a desiccator are convenient titration vessels. Titrate several 10-ml. aliquots of water-methanol solution with the KFR; also titrate several 10-ml. portions of anhydrous methanol to obtain the blank correction. The water-methanol solution is stable if protected from evaporation, and it can be used for back titration of KFR if desired.

By reaction with water, the dark-brown color of iodine in the KFR changes to a canary-yellow color; the end-point color change from yellow to red-brown of excess iodine is sharp and reproducible. Electrometric end points are more sensitive than the visual; the "dead-stop" method, and the potentiometric method using platinum-tungsten bimetallic electrodes, are commonly employed.

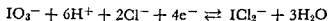
**Against Pure Water.**—Place about 25 ml. of anhydrous methanol in the titration flask and titrate with KFR. From a weight buret accurately weigh about 150 mg. of water into the titrated methanol, and again titrate with KFR.

Several stable crystalline hydrates have been proposed as standards for water.

**Determination of Water.**—The sample is dissolved or suspended in anhydrous methanol and titrated with KFR as in the standardization. Parallel titration of a standard water sample should be made, as well as a blank on the methanol; apply the blank correction to both standard and sample. Several substances interfere with the determination; for details, consult the general references given for this section. For further details on the use of this reagent, see Chapter 21 on The Determination of Water.

## IODATE METHODS <sup>42, 43</sup>

The reaction of potassium iodate as an oxidant is markedly influenced by the nature of the reducing agent and by the solution medium. In the presence of 3 to 9 M hydrochloric acid and strong reducing agents, the reaction proceeds through the formation of iodine monochloride,  $\text{ICl}$ , or its chloro-complex,  $\text{ICl}_2^-$ . The iodine formed in the early stages of titration is oxidized by the iodate to form iodine chloride. The overall half-reaction may be represented by

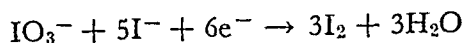


and the equivalent weight of potassium iodate is  $\text{KIO}_3/4 = 53.502$ . The end point in the titration is the disappearance of the iodine color in an immiscible solvent such as carbon tetrachloride or chloroform, or the decolorization of certain organic compounds, often irreversibly, by the first excess of iodate. Many reducing agents can be determined by iodate titration in strong hydrochloric acid solution. In addition, the reaction

<sup>42</sup> Jamieson, G. S., *Volumetric Iodate Methods*, Reinhold Publishing Corp., New York, 1926.

<sup>43</sup> Kolthoff, I. M., and Belcher, R., *op. cit.*, Chap. X.



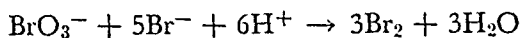


is quantitative with respect to any one of the three reactants when the other two are present in excess. The reaction can be used for the generation of iodine *in situ*. In this reaction the equivalent weight is  $\text{KIO}_3/6 = 35.67$ .

**Preparation of Standard Solution.**—Analytical reagent potassium iodate is suitable for direct use after drying at 160° to 180°C. Weigh the appropriate amount<sup>44</sup> of the dry solid and make to volume with distilled water.

### BROMATE METHODS<sup>45</sup>

The reaction of bromate, which is a strong oxidant, in acid solution gives bromide ion, which is then oxidized by more bromate to give free bromine; the overall reaction can be represented by



Since bromine is itself a good oxidizing agent, a solution of potassium bromate is a convenient source of *in situ* generation of an equivalent amount of bromine. The end point in titrations is the first appearance of free bromine, detected by the irreversible decolorization of certain dyestuffs such as methyl orange or naphthol blue black, or by reversible indicators such as  $\alpha$ -naphthoflavone, *p*-ethoxy-chrysoidine, or quinoline yellow. Potassium bromate is applicable to the titrimetric determination of a large number of inorganic compounds. Bromate-bromide mixtures are used for the titrimetric bromination (substitution) of many organic compounds, such as aniline, phenols, 8-quinolinol, etc. The method is applicable also to the determination of unsaturation in organic compounds by addition of bromine to double bonds.<sup>46</sup>

**Preparation of Standard Solution** ( $\text{KBrO}_3$ , mol. wt. = 167.02; equiv. wt. = 27.84).—Analytical reagent potassium bromate is a suitable primary standard; it should be dried at 180°C. For preparation of a liter of exact 0.1 *N* solution, weigh 2.748 g. of the pure dry compound, and make to volume with water.

<sup>44</sup> For a liter of exactly 0.1 *N* solution, take 5.350 g. for use in strong hydrochloric acid through the iodine chloride reaction; as a source of iodine, take 3.567 g. A solution which is 0.1000 *N* in strong hydrochloric acid is 0.1500 *N* as a source of iodine; or, a solution which is 0.1000 *N* as a source of iodine is 0.0667 *N* for use in strong hydrochloric acid.

<sup>45</sup> Kolthoff, I. M., and Belcher, R., *op. cit.*, Chap. XII.

<sup>46</sup> Polgar, A., and Jungnickel, J. L., in *Organic Analysis*, Vol. 3, Interscience Publishers, Inc., New York, 1956.

## Chapter 13

# ACID-BASE TITRATIONS IN NONAQUEOUS SOLVENTS

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*Introduction.*—Acid-base titrations represent a general and valuable method for determining organic compounds having pronounced acidic or basic properties. Titration of such compounds in water is limited in scope, however, due to slight solubility and because in many cases their acidic or basic strength is too slight to give a sharp end point. Titration in nonaqueous solvents permits accurate determination of literally hundreds of acids and bases which cannot be titrated satisfactorily in water or alcohol-water mixtures. Good methods are now available for titration of most aromatic, aliphatic, and heterocyclic amines as bases and for the titration of carboxylic acids, acid anhydrides, enols, imides, and phenols and even alcohols as acids. Many organic and inorganic salts can be titrated, some as acids and others as bases.

Although the history of acid-base titrations in nonaqueous solvents dates back at least sixty years, the bulk of analytical papers on this subject are of recent publication. Unlike many recent analytical developments, this method is quite simple and requires no elaborate equipment. Indeed titration in nonaqueous solvents possesses the virtues of an ideal analytical method; speed, accuracy, and simplicity of technique and equipment.

Acid-base titrations in either water or nonaqueous media are general and do not ordinarily differentiate between different types of acids or bases. Although a widely applicable method of this type is valuable, it would be useful to make the method more selective in certain instances. This has been accomplished in the analysis of amine mixtures. Tertiary amines can be determined in the presence of primary and secondary amines after acetylation in acetic anhydride-acetic acid solution. Secondary amines can be determined in the presence of primary amines by first treating the mixture with salicylaldehyde.

## DETERMINATION OF AMINES

This procedure can be used to determine aliphatic and aromatic amines and basic nitrogen heterocyclic compounds. The presence of electron-withdrawing groups in an aromatic ring weakens the basic strength of the amine and may prevent its successful titration. Any of the monochloroanilines can be titrated. *m*-

Nitroaniline can be titrated; *p*-nitroaniline can be titrated potentiometrically, although the potentiometric break is not very sharp. *o*-Nitroaniline is too weakly basic to be titrated. Pyridine, quinoline and related compounds, oxazoles, and thiazoles can be titrated; but pyrroles, indoles and certain other nitrogen heterocyclic compounds cannot be determined as bases.

**Reagents and Equipment.** Perchloric Acid, 0.1 *N*.—Add 8.5 ml. of 70 to 72% perchloric acid to about 200 ml. of ACS grade glacial acetic acid in a 1-liter volumetric flask. Add 25 g. of ACS grade acetic anhydride and stopper the flask. After 1 hour, dilute to volume with ACS glacial acetic acid. Standardize against potassium acid phthalate as described in the procedure.

**Crystal Violet Indicator.**—Dissolve 0.2 g. of crystal violet in 100 ml. of glacial acetic acid.

**Solvents.**—Use ACS grade glacial acetic acid or the best available grade of nitromethane or chlorobenzene.

**Titrimeter.**—Use a pH meter on the millivolt scale or other direct-reading titrimeter.

**Electrodes.**—Use an all-purpose glass indicator electrode. Use a fiber-type calomel reference electrode for titrations in nitromethane or acetic acid, and a sleeve-type calomel electrode for titrations in chlorobenzene. Keep electrodes in water when not in use. Wipe the water from the electrodes with paper tissues before using.

**Procedure.**—Dissolve a sample containing 0.4 to 1.0 milliequivalents of amine in 25 ml. of acetic acid, nitromethane, or chlorobenzene and titrate using a 10-ml. buret. Alternatively use a sample containing 2 to 4 milliequivalents of amine and titrate using a 50-ml. buret. Add one or two drops of crystal violet indicator and titrate potentiometrically with 0.1 *N* perchloric acid, plotting the potential in millivolts against the volume of titrant added. Note the indicator color at the point of maximum slope in the potentiometric curve. Subsequent titrations of the same type sample may be carried out visually using this color to determine the end point. If the visual color change is not sharp, carry out subsequent titrations potentiometrically.

Standardize the perchloric acid titrant against primary standard-grade potassium acid phthalate. Dissolve the potassium acid phthalate in glacial acetic acid with gentle boiling to effect solution. Titrate with perchloric acid as described above.

## DETERMINATION OF AMINO ACIDS

**Reagents and Equipment.** Sodium Acetate, 0.1 *N*.—Dissolve 8.2 g. of anhydrous sodium acetate in about 200 ml. of glacial acetic acid, heating if necessary to effect solution. Cool and dilute to 1 liter.

Other reagents and equipment are described under "Determination of Amines."

**Procedure.**—Dissolve an amino acid sample containing 0.4 to 0.8 milliequivalent of basic nitrogen in exactly 10.00 ml. of 0.1 *N* perchloric acid. Alternatively dissolve a sample containing 2 to 3 milliequivalents of basic nitrogen in exactly 50.00 ml. of 0.1 *N* perchloric acid. Add one or two drops of crystal violet indicator and back-titrate the excess perchloric acid with 0.1 *N* sodium acetate. Take the first permanent violet tinge of the indicator as the end point. The sodium acetate titration may also be carried out potentiometrically using glass and calomel electrodes.

## DETERMINATION OF WEAK TERTIARY AMINES

**Reagents and Equipment.** Perchloric Acid, 0.1 *N*.—Prepare a solution in glacial acid as described under "Determination of Amines." Standardize against potassium acid phthalate according to that same procedure.

**Triphenylmethanol Indicator.**—Dissolve 0.1 g. of triphenylmethanol in 100 ml. of nitromethane.

**Solvents.**—Use ACS grade acetic acid and acetic anhydride. Use the best available grade nitromethane.

**Titrimeter.**—Use a pH meter on the millivolt scale or other direct-reading titrimeter.

**Electrodes.**—Use an all-purpose glass indicator electrode and fiber-type calomel reference electrode.

**Procedure.**—Dissolve a sample containing 0.4 to 1.0 milliequivalent of base in 25 ml. of 4 to 1 nitromethane-acetic anhydride. If the sample is not readily soluble in this solvent mixture, dissolve instead in a small volume of acetic acid, heating if necessary. Then add nitromethane-acetic anhydride. Titrate potentiometrically with 0.1 *N* perchloric acid, adding the titrant from a 10-ml. buret. Plot the potential in millivolts against the volume of titrant added; take the point of maximum slope in the potentiometric curve as the end point.

A solvent blank must be determined to correct for the titrant required to bring the solvent mixture to the equivalence point potential of the sample. This usually amounts to 0.01 to 0.05 ml. and is subtracted from the volume of perchloric acid required to titrate the sample.

Many compounds can be titrated visually using two drops of triphenylmethanol indicator. To check whether this is possible for a given compound, first titrate a sample potentiometrically with indicator added. If the color change coincides with the potentiometric end point, a visual titration of that compound is possible.

## DETERMINATION OF AMINE SALTS

This procedure is applicable to the titration of amine salts, provided the salt can be dissolved in glacial acetic acid. Amine nitrates are titrated to form nitric acid as a neutralization product; amine sulfates are titrated to the bisulfate. Amine hydrohalides can be titrated only if mercuric acetate is added before titration.

**Reagents and Equipment.** 1,4-Dioxane.—To 1 liter of "purified" 1,4-dioxane, add about 15 g. of air-dried cation exchange resin (sulfonic acid type) in the hydrogen form. Shake occasionally over a period of several hours. Filter off the resin and use the resulting solvent in the preparation of the perchloric acid titrant. (This treatment prevents the formation of a deep-brown color when perchloric acid is mixed with dioxane.)

**Perchloric Acid, 0.1 *N*.**—Dissolve 8.5 ml. of 70 to 72% perchloric acid in 1 liter of 1,4-dioxane that has been shaken with ion exchange resin. Standardize the perchloric acid by titration of primary standard grade potassium acid phthalate in glacial acetic acid (see Procedure under "Determination of Amines").

**Mercuric Acetate.**—Dissolve 6 g. of mercuric acetate in 100 ml. of hot glacial acetic acid and cool to room temperature.

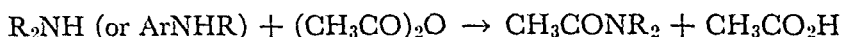
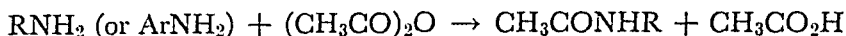
**Titrimeter.**—Use a pH meter on the millivolt scale or other direct-reading titrimeter.

**Electrodes.**—Use an all-purpose glass indicator electrode and a sleeve-type calomel reference electrode. If the calomel electrode becomes contaminated with mercuric acetate and causes erratic potential readings, remove the electrolyte, rinse with water, then with saturated potassium chloride solution, and refill with saturated potassium chloride.

**Procedure.**—Dissolve in 20 ml. of glacial acetic acid a finely powdered sample that will require 4 to 9 ml. of 0.1 *N* perchloric acid for titration. Heat to dissolve the sample if necessary. Alternatively dissolve a sample that will require 20 to 40 ml. of 0.1 *N* perchloric acid for titration in 80 ml. of glacial acetic acid. If the salt is a hydrohalide, add 2.5 ml. of mercuric acetate solution for each 20 ml. of glacial acetic acid used to dissolve the sample. Titrate potentiometrically with 0.1 *N* perchloric acid, plotting the potential in millivolts against the volume of titrant.

### DETERMINATION OF TERTIARY AMINES

This procedure is used to determine tertiary amines in samples that also contain primary and secondary amines. Most of the basic nature of primary and secondary amines is destroyed by acetylation.



The tertiary amine is not affected by acetic anhydride and can be titrated with perchloric acid in glacial acetic acid.

**Reagents and Equipment.** Perchloric Acid, 0.1 *N*.—Prepare and standardize a solution in glacial acetic acid as described under "Determination of Amines."

**Titrimeter.**—Use a pH meter on the millivolt scale or other direct reading titrimeter.

**Electrodes.**—Use an all-purpose glass indicator electrode and a fiber-type calomel reference electrode.

**Procedure.**—Weigh a sample that contains not more than 1 milliequivalent of tertiary amine and not more than 0.5 g. of water into a 5-in. test tube. Cool in an ice bath and add with swirling 5 ml. of ACS grade acetic anhydride. Stopper the test tube loosely, remove from the ice bath, and allow to stand one-half hour at room temperature. Sterically hindered amines may require a longer reaction period or heating for acetylation to be complete. Rinse the contents of the test tube into a titration vessel with 25 ml. of glacial acetic acid. Titrate the tertiary amine potentiometrically with 0.1 *N* perchloric acid. Determine the end point of the titration by plotting the potential in millivolts against the volume of perchloric acid titrant. Determine the volume of 0.1 *N* perchloric acid to titrate a solvent blank to the equivalence point potential of the sample, and subtract from the volume of acid required to titrate the sample.

### DETERMINATION OF CARBOXYLIC ACIDS

**Reagents and Equipment.** Sodium Methoxide, 0.1 *N*.—Add 50 ml. of absolute methanol and 50 ml. of dry benzene to a 2-l. flask and cover the flask with a small watch glass. Freshly cut about 5 g. of sodium metal, wash by brief immersion in methanol, then add it to the flask containing the benzene and methanol. If the

reaction of sodium with the methanol becomes too vigorous, cool the flask by immersion in an ice bath; if the reaction becomes too slow, add more methanol. When the sodium has completely dissolved, add 200 ml. additional methanol and dilute to 1.5 L. with dry benzene. Standardize the sodium methoxide by titration of pure benzoic acid according to the procedure given below.

**Azo Violet Indicator.**—Prepare a saturated solution of *p*-nitrobenzeneazoresorcinol in benzene.

**Thymol Blue Indicator.**—Dissolve 0.3 g. of thymol blue in 100 ml. of methanol.

**Benzene-methanol.**—Mix 4 volumes of benzene with 1 volume of methanol.

**Dimethylformamide.**—Use reagent grade if available. The commercial solvent may be purified by passage through a column of activated alumina.

**Buret.**—Use a 10-ml. buret that can be read accurate to  $\pm 0.01$  ml. or better.

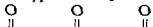
**Titration Vessel.**—Use a flask with a 1-hole cover that will admit the buret tip but will protect the solution from carbon dioxide in the air. Titration under nitrogen is desirable.

**Procedure.**—Dissolve a sample containing 0.4 to 0.8 milliequivalent of acid in 50 ml. of dimethylformamide or benzene-methanol. Add two drops of thymol blue indicator and titrate with 0.1 N sodium methoxide to a clear blue end point. If dimethylformamide solvent is used, add two drops of thymol blue to 25 ml. of solvent and neutralize to a clear blue color. Immediately add the sample and titrate as above. Subtract the solvent blank from the final buret reading.

Some dibasic acids are too weak to give a sharp thymol blue end point. In such cases, add two drops of azo violet indicator and titrate the sample to a clear blue color in dimethylformamide. Determine the solvent blank using azo violet indicator.

## DETERMINATION OF ORGANIC ACIDS

This procedure can be used to determine virtually any organic compound that is soluble in one of the solvents recommended and is sufficiently acidic to be titrated as an acid. Specifically, the following types of compounds can be determined: Carboxylic acids, phenols, enols of the type  $A-CH_2-A'$  and imides of the type  $A-NH-A'$  (where



or  $-\text{C}\equiv\text{N}$ ), sulfonamides of the type  $\text{ArSO}_2\text{NH}-$ , and certain nitro aromatic amines.<sup>1</sup> In many instances, mixtures of acidic organic compounds can be analyzed by differentiating potentiometric titrations.<sup>2</sup>

**Reagents and Equipment.** **Tetrabutylammonium Hydroxide, 0.1 N.**—Dissolve 40 g. of pure tetrabutylammonium iodide in 50 ml. of absolute methanol in a glass-stoppered flask. Cool the solution in an ice bath, then add 20 g. of reagent grade silver oxide. Immediately restopper the flask and shake vigorously for a minute or two. Continue to cool the flask in an ice bath; shake vigorously from time to time during a period of 1 hour. Filter the solution under nitrogen; wash the precipitate with 50 ml. of absolute methanol added in two or three portions. Dilute the combined filtrate and washings to 1 liter with dry benzene. Flush the solution for 5 minutes with purified nitrogen and store in a reservoir protected from carbon dioxide and moisture. Standardize the tetrabutylammonium hydrox-

<sup>1</sup> Fritz, J. S., Moye, A. J., and Richard, M. J., *Anal. Chem.*, **29**, 1685, 1957.

<sup>2</sup> Fritz, J. S., and Yamamura, S. S., *Anal. Chem.*, **29**, 1079, 1957.

ide solution by titration of pure benzoic acid according to the procedure described below.

**Acetone.**—Use reagent grade from a fresh or recently opened bottle.

**Pyridine.**—Reagent grade pyridine may be used without purification. If technical grade pyridine is used, add sodium hydroxide pellets, let the pyridine stand overnight, then flash distill.

**Dimethylformamide.**—Purify the commercial solvent by passage through a column of activated alumina.

**Titrimeter.**—Use a pH meter on the millivolt scale or some other direct-reading titrimeter.

**Electrodes.**—Use an all-purpose glass indicator electrode. Use a sleeve-type calomel reference electrode in which the aqueous potassium chloride solution in the outer jacket is replaced with a saturated solution of potassium chloride in methanol. For titrations in acetone or dimethylformamide, a fiber-type calomel electrode, modified as above, may be used.

**Titration Vessel.**—Use a tall-form beaker with a cover that will admit the buret tip and electrodes but will protect the solution from carbon dioxide in the air. Titration under nitrogen is desirable.

**Buret.**—Use a 10-ml. buret that can be read accurately to  $\pm 0.01$  ml. or better.

**Procedure.**—Dissolve a sample containing 0.4 to 1.0 milliequivalent of acid in 40 ml. of nonaqueous solvent. Pyridine is the most generally useful solvent, but acetone is very convenient for titration of most carboxylic acids, enols, imides, sulfonamides, and many phenols. Dimethylformamide will dissolve some types of compounds that are sparingly soluble in other organic solvents. Titrate potentiometrically, plotting the potential in millivolts against the volume of tetrabutylammonium hydroxide added. When there are two or more inflections in the titration curve, use the difference between successive end points to calculate the volume of titrant equivalent to the acid titrated.

Determine the solvent blank(s) by potentiometric titration. Subtract the volume of titrant required to titrate the solvent to the equivalence point potential(s) of the acid(s) titrated.

## Chapter 14

# DETERMINATION OF pH BY THE COLORIMETRIC METHOD

Based on earlier contribution

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The colorimetric method of measuring hydrogen ions has many advantages that appeal to practical workers. It is rapid and simple in operation and compared to other methods very inexpensive. The entire pH range or any portion of it can be covered by means of portable equipment for use in factory or field. The difficulties are such as can invariably be remedied. For these reasons the colorimetric method is now being used for investigation and control in every field where the determination of hydrogen ions (protons)\* is important.

By mutual agreement the hydrogen electrode is regarded as the fundamental standard in all determinations of hydrogen ion. All other methods are secondary whether potentiometric (quinhydrone electrode, glass electrode, antimony electrode) or colorimetric. All such methods must be standardized against the hydrogen electrode.

### BUFFER ACTION

In the case of a solution of a single pure acid or alkali, if the concentration and degree of ionization (real or apparent) are known, the pH can be calculated from the ionization alone. In actual practice such a situation will rarely arise. Invariably solutions contain more than one substance. Frequently some of these substances form what is known as a buffer system and serve to modify and stabilize the pH.

When 1 ml. of 0.01 *N* HCl is added to 1 liter of pure water of pH 7.0, the pH will drop to about pH 5.0. If however the same amount of acid were added to a solution containing a mixture of  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  of pH 7.0 the drop in pH would be very small. This is illustrated by the curves on page 286. The phosphate mixture has the ability to resist change in pH on addition of acid or alkali. It has what is called buffer action and such a mixture constitutes a buffer

\* In this discussion, the term "hydrogen ion" has been used throughout for proton, since the emphasis upon ionization processes indicates that the use of the older term clarifies the discussion. For the same reason, concentration is stressed rather than activity.



system or mixture. Such action is encountered in numerous solutions found in nature and in industrial processes. All mixtures of weak acids and their salts or of weak bases and their salts are buffer mixtures. Some of the most common buffer mixtures are acetic acid-acetate, carbonic acid ( $\text{CO}_2$ )-bicarbonate, citric acid-citrate, mixed phosphates, etc. Other common buffering substances are proteins (gelatin, casein, etc.).

The mechanism of buffer action is most easily shown by means of the acetic acid acetate system. In a solution of acetic acid dissociation occurs only to a small extent as follows,  $\text{HOAc} \rightleftharpoons \text{H}^+ + \text{OAc}^-$ . Sodium acetate, however dissociates practically completely,  $\text{NaOAc} \rightleftharpoons \text{Na}^+ + \text{OAc}^-$  and yields a large number of acetate ions  $[\text{OAc}^-]$ . A 0.1 *N* solution of acetic acid has pH 2.89 but a solution 0.1 *N* with respect to both acetic acid and sodium acetate has pH 4.63. The pH has been increased, i.e., the H ion concentration has been lowered. The question arises as to what has become of the H ions. The mass law equation for acetic acid is  $\frac{[\text{H}^+][\text{OAc}^-]}{[\text{HOAc}]} = K_a$ , where  $K_a$  is the ionization constant. If any one of the three concentrations be changed there must be a change in the others else  $K_a$  could not remain constant. In the case just cited the acetate ion concentration  $[\text{OAc}^-]$  has been enormously increased so the H ion concentration  $[\text{H}^+]$  has to decrease. The unionized acetic acid will automatically become greater so practically what occurs is that more inactive (unionized) acetic acid is formed removing H ions from the solution. In this system the concentrations of acetate ion  $[\text{OAc}^-]$  and unionized acetic acid  $[\text{HOAc}]$  are always extremely large compared to the concentration of H ions  $[\text{H}^+]$  so that the ratio  $\frac{[\text{OAc}^-]}{[\text{HOAc}]}$  partially determines the reaction or pH. This is important when dilution is necessary.

If small amounts of a strong acid (hydrochloric) be added to the system, the large concentration of acetate ions quickly converts most of the H ions added to unionized acetic acid and  $[\text{H}^+]$  increases only slightly. If a base (sodium hydroxide) is added H ions are neutralized but more acetic acid is ionized producing additional H ions to take the place of those neutralized and  $[\text{H}^+]$  decreases only slightly. Of course any buffer system has its limits and large amounts of acid or base will overcome the buffer capacity. Each buffer system has a rather narrow pH zone over which it functions. However, by using different systems, i.e., different mixtures, practically the entire pH range can be covered. This is extremely advantageous since it is possible to prepare solutions of constant pH which serve as standards and it also serves as a means of holding an industrial solution close to the optimum pH. In the case of fairly concentrated solutions of strong acids and bases, since the concentration of unionized substance is relatively small, there is no reserve supply of H or OH ions. However, there is such a large concentration of H or OH ions that for practical purposes such systems function as buffer systems. For example, when the concentration of either 0.1 *N* HCl or 0.1 *N* NaOH is reduced to 0.01 *N*, the pH is changed only about 1 unit.

The stability of any buffer system will depend on total concentration, and the ratio of salt to weak acid or base. Reasonable changes in concentration will not materially change the pH as long as the ratio remains the same. In the acetate system the ratio  $\frac{[\text{OAc}^-]}{[\text{HOAc}]}$  does not change on moderate dilution and the change in pH when the system 0.1 *N* acetic acid - 0.1 *N* sodium acetate is diluted twenty fold is less than 0.1 pH. Many solutions met with in practice are buffered. This

is an advantage since colorimetric pH measurements can be made on such solutions even when highly colored or turbid by diluting with distilled water. The degree of dilution possible depends on the concentration and the specific buffer system but the safest procedure is to dilute only as far as necessary to make satisfactory readings.

Buffer action can be illustrated graphically by means of titration curves (Fig. 14-1). Three such curves are shown in which various amounts of 0.2 *M* HCl and

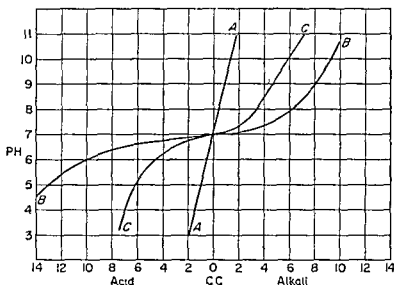


FIG. 14-1.

0.2 *M* NaOH are added to 100 ml. samples of (A) distilled water, (B) a buffer mixture composed of  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  in which the total concentration is approximately 0.1 *M*, and (C) a similar buffer mixture in which the total concentration is one-half of B, all samples having an initial pH of 7.0. The abscissa show the amounts of acid or alkali added and the ordinates show the pH of the respective mixtures.

The extremely steep curve (A) for distilled water shows that this substance is devoid of buffer action since small amounts of acid or alkali change the pH markedly. In the pronouncedly acid and alkaline ranges the curve flattens out because one is then dealing with relatively concentrated solutions of the strong acid and base, where pH varies only moderately with concentration.

The curve (B) for the 0.1 *M* phosphate mixture differs radically from (A). Addition of 11 ml. of acid only changes the pH from 7.0 to 5.8, whereas the addition of 6 ml. of alkali only changes the pH from 7.0 to 7.8. Beyond these points the change becomes more pronounced. Between 5.8 and 7.8 the curve is relatively flat and in this zone the phosphate mixture shows strong buffer action. As the curve indicates, buffer action is strongest near the middle of the relatively flat portion. It actually reaches a maximum at about 6.8 where the concentrations of  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  are the same, i.e.  $\frac{[\text{Na}_2\text{HPO}_4]}{[\text{KH}_2\text{PO}_4]} = 1$ . The steepness of the curve above and below the zone 5.8–7.8 indicates little resistance to change in pH.

Curve (C) resembles (B) in contour but the relatively flat portion or zone of effective buffer action is much shorter, extending only from about 6.5 to 7.5. This shows the effect of concentration on buffer action.

These curves show that not all buffer mixtures have the same buffer capacity. Van Slyke (*J. Biol. Chem.*, 52, 525, 1922) has formulated a method of expressing the differences in terms of buffer capacity. A solution has a buffer capacity of 1 when the reaction of a liter of it is changed one pH unit upon the addition of one equivalent of acid or base. A knowledge of the buffer capacity of a solution is frequently of considerable value since it indicates how easily the optimum pH may be maintained in practice, and also what precautions are necessary in determining the pH. It also provides a practical method of determining the amount of acid or alkali required to adjust the pH.

The requirements for buffer action should be clearly kept in mind. Mere presence of salts does not ensure buffer action. Salts of strong acids and strong bases impart no buffer action to a solution. Solutions which contain only salts of weak acids and weak bases may not be buffered. To ensure buffer action a buffer system must be present, i.e., both salt and weak acid or weak base and the pH of the solution must be within the effective zone of the particular system.

Tables showing the method of preparation for various buffer mixtures can be found in Clark, *The Determination of Hydrogen Ions*, 1928, Williams and Wilkins, Baltimore, Md.

The following table gives some common buffer systems and the approximate pH of maximum buffer capacity. The zone of effective buffer action will vary with concentration but the general average will be  $\pm 1.0$  pH from the value given, for concentrations approximately 0.1 M.

Glycine-sodium chloride-hydrochloric acid.....	2.0
Potassium acid phthalate-hydrochloric acid.....	2.8
Primary potassium citrate.....	3.7
Acetic acid-sodium acetate.....	4.6
Potassium acid phthalate-sodium hydroxide.....	5.0
Secondary sodium citrate.....	5.0
Carbonic acid-bicarbonate.....	6.5
Primary phosphate-secondary phosphate.....	6.8
Primary phosphate-sodium hydroxide.....	6.8
Boric acid-borax.....	8.5
Borax.....	9.2
Boric acid-sodium hydroxide.....	9.2
Bicarbonate-carbonate.....	10.2
Secondary phosphate-sodium hydroxide.....	11.5



### THE USE OF INDICATORS

For making pH determinations substances known as indicators are required. An indicator is a substance that gives different colors or different shades of color at different pH values. Thus, phenol red changes from yellow at pH 6.8 to a deep red at pH 8.4; that is, if phenol red is added to a solution having a pH of 6.8 it will give this solution a yellow color. If added to another solution of pH 7.0 it will give a somewhat redder shade of yellow. If added to other solutions having pH values of 7.2, 7.4, 7.6, etc. the amount of red color imparted to the solution will increase progressively until at pH 8.4 the solution will have a deep red color.

Therefore if phenol red is added to any solution having a pH value between 6.8 and 8.4, the pH of that solution is determined by observing the color obtained. The method for accurately reading the pH value is explained later in this section.

Phenol red covers only a limited part of the pH scale but other indicators are available for other parts. Thus bromcresol green covers the range pH 3.8-5.4 and its color change is from yellow at pH 3.8 to blue at pH 5.4. Thymol blue covers the range pH 8.0-9.6 and its color change is from yellow at pH 8.0 to blue at pH 9.6. A list of indicators that cover the pH scale 0.1 to 14, with their pH ranges and color changes, is given in the table beginning on page 289.

The "pH" in the column "Preparation" designates that the indicator solution prepared as directed is recommended for measuring the hydrogen ion concentration only. The designation "vol." signifies that the indicator solution is intended for volumetric (titrimetric) analysis; the designation "pH, vol." indicates that the solution is applicable for the determination of hydrogen ion concentration as well as for volumetric (titrimetric) analysis.

The water used for preparing indicator solutions is to be freed from carbon dioxide by thoroughly boiling it out in resistant glass or in porcelain. Similarly the alcohol used for making the indicator solution should be neutral.

When the indicator solution is to be prepared with the aid of 0.02 *N* sodium hydroxide, triturate well the quantity of the indicator material with the volume of the 0.02 *N* NaOH in an agate mortar, and then dilute with carbon-dioxide-free water to the volume indicated.

Indicators are weak acids or bases in which the ionized form differs in constitution and color from the normal form. An indicator acid will dissociate as  $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$ , HIn being the acid form and  $\text{In}^-$  the alkaline form. The mass law expression will be  $\frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]} = K_I$ . Then  $\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{K_I}{[\text{H}^+]}$ . Since  $K_I$  is a con-

stant the ratio  $\frac{[\text{In}^-]}{[\text{HIn}]}$  will depend on the value of  $[\text{H}^+]$ , the hydrogen ion concentration. This ratio determines the color that the indicator will show. For example with phenol red the acid form [HIn] is yellow and the alkaline form  $[\text{In}^-]$  is red, consequently as  $[\text{In}^-]$  increases the color changes from yellow through orange to red. When HIn is half transformed  $[\text{HIn}] = [\text{In}^-]$  and so  $[\text{H}^+] = K_I$ . When the hydrogen ion concentration is the same as the ionization constant of the indicator, the concentrations of the acid and alkaline forms of the indicator are equal. The value of  $K_I$  varies for different indicators and determines the range of hydrogen ion concentration over which each indicator

functions. If  $[\text{H}^+] = K_I$  then  $\text{pH} = \text{p}K_I$ , where  $\text{p}K_I = \log \frac{1}{K_I}$ . While this determines the theoretical midpoint of the pH range of each indicator, the actual range used in practice depends on how readily the colors can be distinguished by the eye. Consequently, the practical range is determined experimentally. While  $\text{p}K_I$  is a function of pH, it is also affected to some extent by other factors, such as salt concentrations, proteins and temperature.

A satisfactory indicator for practical pH work must have certain well defined qualifications. It must give well-defined color changes over a relatively short range; it must not be unduly affected by substances other than hydrogen or hydroxyl ions; it must immediately give colors that are stable for a reasonable length of time, so that there will be no errors due to changes taking place during the determination; its solution must be a stable reagent. An indicator that fades rapidly,

Indicator	Range	Preparation
METHYL VIOLET.....	Yellow 0.1–1.5 blue	pH: 0.25 g. in 100 ml. of water
METACRESOL PURPLE.....	Red 0.5–2.5 yellow	pH: 0.10 g. in 13.6 ml. of 0.02 N NaOH and dilute with water to 250 ml.
<i>m</i> -Cresolsulfonphthalein (acid range)		
<i>p</i> -XYLENOL BLUE.....	Red 1.2–2.8 yellow	pH: 0.10 g. in 250 ml. of al- cohol
1,4-dimethyl-5-hydroxyben- zenesulfonphthalein (acid range)		
THYMOL BLUE.....	Red 1.2–2.8 yellow	pH: 0.10 g. in 10.75 ml. of 0.02 N NaOH, and dilute with water to 250 ml.
Thymolsulfonphthalein (acid range)		
TROPAEOLIN OO.....	Red 1.3–3.0 yellow	pH, vol.: 0.10 g. in 100 ml. of water
Sodium- <i>p</i> -diphenylamineazo- benzenesulfonate		
QUINALDINE RED.....	Colorless 1.4–3.2 red	vol.: 0.1 g. in 100 ml. of alcohol
2-( <i>p</i> -Dimethylaminostyryl)- quinoline ethionide		
BENZOPURPURINE 4B.....	Blue-violet 1.3–4.0 red	pH, vol.: 0.10 g. in 100 ml. of water
METHYL VIOLET.....	Blue 1.5–3.2 violet	pH, vol.: 0.25 g. in 100 ml. of water
ALIZARIN YELLOW R ( <i>p</i> ).....	Red 1.9–3.3 yellow	pH, vol.: 0.10 g. in 100 ml. of warm water
Sodium <i>p</i> -nitrobenzeneazo- salicylate		
2,4-DINITROPHENOL ( $\alpha$ ).....	Colorless 2.6–4.0 yellow	pH, vol.: 0.10 g. in a few ml. of alcohol, then dilute with water to 100 ml.
METHYL YELLOW.....	Red 2.8–4.0 yellow	pH, vol.: 0.10 g. in 100 ml. of alcohol
<i>p</i> -Dimethylaminoazobenzene		
BROMPHENOL BLUE.....	Yellow 3.0–4.6 blue	pH: 0.10 g. in 7.45 ml. of 0.02 N NaOH and dilute with water to 250 ml.
Tetrabromophenolsulfon- phthalein		vol.: 0.1 g. in 250 ml. of alcohol
CONGO RED.....	Blue 3.0–5.2 red	pH, vol.: 0.10 g. in 100 ml. of water
METHYL ORANGE.....	Red 3.1–4.4 yellow	vol.: 0.2 g. in 100 ml. of hot water
Sodium- <i>p</i> -dimethylamino- benzenesulfonate, Helianthin		pH: 0.10 g. in 8.6 ml. of 0.02 N NaOH, then dilute with water to 250 ml.
BROMCHLOROPHENOL BLUE.....	Yellow 3.2–4.8 blue	vol.: 0.1 g. in 250 ml. alcohol
Dibromodichlorophenolsul- fonphthalein		pH, vol.: 1.0 g. in 100 ml. of water
SODIUM ALIZARIN SULFONATE...	Yellow 3.7–5.2 violet	vol.: 0.10 g. in 100 ml. of ether saturated with water
IODEOSIN.....	Yellow 0–about 4 rose red	pH, vol.: 0.1 g. in 20 ml. of alcohol, then dilute with water to 100 ml.
Tetraiodofluorescein		
2,5-DINITROPHENOL ( $\gamma$ ).....	Colorless 4–5.8 yellow	

Indicator	Range	Preparation
BROMCRESOL GREEN ..... Tetrabromo- <i>m</i> -cresolsulfon- phthalein, Bromcresol Blue	Yellow 3.8-5.4 blue	pH: 0.10 g. in 7.15 ml. of 0.02 N NaOH and dilute with water to 250 ml. vol.: 0.1 g. in 250 ml. alcohol
METHYL RED ..... Dimethylaminoazobenzene- <i>o</i> -carboxylic acid ( <i>o</i> -Carboxybenzeneazodi- methylaniline)	Red 4.2-6.2 yellow	pH: 0.10 g. in 18.6 ml. of 0.02 N NaOH and dilute with water to 250 ml. vol.: 0.20 g. in 100 ml. hot water
LACMOID. ....	Red 4.4-6.2 blue	vol.: 0.5 g. in 100 ml. alcohol
AZOLITMIN. ....	Red 4.5-8.3 blue	vol.: 0.5 g. in 80 ml. of warm water, then add 20 ml. of alcohol
COCHINEAL.....	Red 4.8-6.2 violet	vol.: Triturate 1 g. with 25 ml. alcohol and 75 ml. of water, let stand for 2 days and filter
HEMATOXYLIN ... ..	Yellow 5.0-6.0 violet	vol.: 0.5 g. in 100 ml. alcohol
CHLORPHENOL RED ..... Dichlorophenolsulfon- phthalein	Yellow 4.8-6.4 red	pH: 0.10 g. in 11.8 ml. of 0.02 N NaOH and dilute with water to 250 ml. vol.: 0.1 g. in 100 ml. 20% alc.
<i>p</i> -NITROPHENOL.....	Colorless 5.6-7.6 yellow	pH, vol.: 0.25 g. in 100 ml. water
BROMCRESOL PURPLE..... Dibromo- <i>o</i> -cresolsulfon- phthalein	Yellow 5.2-6.8 purple	pH: 0.10 g. in 9.25 ml. of 0.02 N NaOH and dilute with water to 250 ml. vol.: 0.05 g. in 200 ml. alcohol
BROMPHENOL RED.....	Yellow 5.2-7.0 red	pH: 0.10 g. in 9.75 ml. of 0.02 N NaOH and dilute with water to 250 ml. vol.: 0.1 g. in 250 ml. alcohol
ALIZARIN. . . . .	Yellow 5.5-6.8 red	vol.: 0.1 g. in 100 ml. alcohol
Dihydroxyanthraquinone		
BROMTHYMOL BLUE ... .. Dibromothymolsulfon- phthalein	Yellow 6.0-7.6 blue	pH: 0.10 g. in 8.0 ml. of 0.02 N NaOH and dilute with water to 250 ml. vol.: 0.10 g. in 100 ml. of 20% alcohol
CURCUMIN.....	Yellow 6-8.0 brown- ish red	A saturated aqueous solution
PHENOL RED.....	Yellow 6.8-8.0 red	pH: 0.10 g. in 14.20 ml. of 0.02 N NaOH and dilute with water to 250 ml. vol.: 0.1 g. in 100 ml. 20% alcohol
Phenosulfonphthalein		
NEUTRAL RED.....	Red 6.8-8.0 yellow	pH, vol.: 0.10 g. in 60 ml. al- cohol and dilute with water to 100 ml.
Methyl-amino-dimethyl- amino-phenazine		

Indicator	Range	Preparation
ROSOLIC ACID..... Aurin; Corallin	Yellow 6.8-8.2 red	pH: vol.: 1.0 g. in 100 ml. of 50% alcohol
CYANIN.....	Colorless 7.0-8.0 violet-blue	pH: 1.0 g. in 100 ml. alcohol
CRESOL RED..... <i>o</i> -Cresolsulfonphthalein (alkaline range)	Yellow 7.2-8.8 red	pH: 0.10 g. in 13.1 ml. of 0.02 <i>N</i> NaOH and dilute with water to 250 ml. vol.: 0.1 g. in 100 ml. 20% alc.
$\alpha$ -NAPHTHOLPHTHALEIN.....	Rose 7.3-8.7 green	pH: vol.: 0.10 g. in 100 ml. of 50% alcohol
METACRESOL PURPLE..... <i>m</i> -Cresolsulfonphthalein (alkaline range)	Yellow 7.4-9.0 purple	pH: 0.10 g. in 13.1 ml. 0.02 <i>N</i> NaOH and dilute with water to 250 ml. vol.: 0.1 g. in 100 ml. alcohol
THYMOL BLUE..... Thymolsulfonphthalein (alkaline range)	Yellow 8.0-9.6 blue	pH: 0.10 g. in 10.75 ml. of 0.02 <i>N</i> NaOH and dilute with water to 250 ml. vol.: 0.1 g. in 100 ml. 20% alc.
<i>p</i> -XYLENOL BLUE..... 1,4-Dimethyl-5-hydroxybenzenesulfonphthalein (alkaline range)	Yellow 8.0-9.6 blue	pH, vol.: 0.10 g. in 250 ml. alcohol
TROPAEOLIN OOO..... Sodium $\alpha$ -naphtholazo-benzenesulfonate	Yellow 7.6-8.9 red	vol.: 0.1 g. in 100 ml. water
<i>o</i> -CRESOLPHTHALEIN.....	Colorless 8.2-10.4 red	pH: 0.10 g. in 250 ml. alcohol
$\alpha$ -NAPHTHOLBENZENE.....	Yellow 8.5-9.8 green	pH: 1.0 g. in 100 ml. alcohol
PHENOLPHTHALEIN.....	Colorless 8.2-9.8 red	vol.: 1.0 g. in 100 ml. 80% alc.
THYMOLPHTHALEIN.....	Colorless 9.3-10.5 blue	pH, vol.: 0.10 g. in 100 ml. alcohol
ALIZARIN YELLOW GG..... Salicyl Yellow, Sodium <i>m</i> -nitrobenzeneazosalicylate	Yellow 10.1-12.0 lilac	pH: 0.10 g. in 100 ml. of 50% alcohol
POIRRIER BLUE C4B.....	Blue 11-13.0 red	pH: 0.2 g. in 100 ml. water
TROPAEOLIN O..... <i>p</i> -Benzenesulfonic acid-azoresorcinol	Yellow 11-13.0 orange	pH: 0.10 g. in 100 ml. of water
NITRAMINE..... 2,4,6-Trinitrophenylmethyl-nitroamine	Yellow 11.0-13.0 orange-brown	pH: 0.10 g. in 100 ml. 70% alcohol
1,3,5-TRINITROBENZENE.....	Colorless 11.5-14.0 orange	pH: 0.10 g. in 100 ml. alcohol
SODIUM INDIGO DISULFONATE... Indigo Carmine	Blue 11.6-14.0 yellow	pH: 0.25 g. in 100 ml. of 50% alcohol

precipitates, undergoes change in color due to the presence of salts, colloidal materials, etc., attains a stable color slowly, or is unstable as a reagent, is certain to prove objectionable in practice.

The essential requirements in applying the colorimetric method for the determination of pH are (1) An accurately prepared solution of indicator, (2) a set of color standards prepared from measured amounts of buffer solutions having accurately adjusted pH values and containing accurately measured amounts of the indicator solution. Standards in intervals of 0.2 pH are usually employed. Such a set for phenol red will consist of standards with the pH values 6.8, 7.0, 7.2, 7.4, 7.6, 7.8, 8.0, 8.2 and 8.4. These standards can be placed in test tubes or ampoules having uniform bores. Ampoules are more satisfactory since they can be sealed.

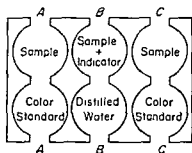


FIG. 14-2.

If a measured volume of clear sample is treated with the same amount of indicator as is present in the standards, the resulting color will depend on the pH of the sample and by comparing this color with the color standards the pH can be determined. It is essential that all measurements be accurate and that the bore of the color standards and test tube used for the sample be practically the same. The intensity of color and depth of liquid in both cases should be uniform.

If the materials being tested are *absolutely* clear and colorless accurate determinations can be made by comparing the color of the test sample with those of the color standards, as outlined above. Most solutions encountered in actual practice are, however, somewhat turbid or colored or both. Therefore when an indicator solution is added to such a material the resulting color will not match with the color standards which contain none of the color or turbidity of the sample. For this reason some sort of comparator is required. In fact all determinations should be made with a comparator since the presence of even minute quantities of color or turbidity may cause considerable error or even prevent a match all together when an attempt is made to match the sample directly with the color standards. The procedure employed in all comparators is essentially the same so the Slide Comparator will be used to illustrate the principle.

In making a determination three of the test tubes are filled to the mark (5 ml.) with the material to be tested and 0.5 ml. of the indicator solution is added to the middle tube. The color standards are then moved back and forth in front of the test sample, always making sure that, when a comparison is made, one of the ampoules of distilled water is in front of the middle test tube containing the indicator. Two consecutive color standards will then be directly in front of the two tubes of test sample containing no indicator. The arrangement of the three tubes of test sample, the two color standards and the ampoule of distilled water is illustrated in Fig. 14-2.

AA, BB, CC represent the three slots in the base and any three corresponding slots in the color standard slide. If we consider the color standards as consisting of distilled water and indicator only, which is permissible since they contain no turbidity and no color except that given them by the indicator, it is clear that on looking through slots AA, BB, and CC, one is looking through exactly the same materials—sample, indicator, distilled water—in each case. This arrangement therefore eliminates any effect of color or turbidity in the sample so that, when



the proper color standards are in place, the color of the sample will match one of the color standards or lie between the colors of two consecutive standards.

Readings should never be made by matching against either end standard in a given set. Thus a sample may match the bromthymol blue color standard marked pH 6.0 and actually have a pH value of 5.0, 4.2, etc. If a match with the standard marked 6.0 is obtained the determination should be repeated using an indicator covering a lower part of the pH scale, for example, chlorphenol red (pH 5.2–6.8), bromcresol green (pH 3.8–5.4), etc., until a match is obtained with a standard other than the end one. Similarly if a sample matches the bromthymol blue standard marked 7.6, the test should be repeated using phenol red (pH 6.8–8.0) or a higher indicator if necessary.

The table on page 290 shows that the ranges of the various indicators overlap. Thus the values pH 6.0–6.8 are common to both phenol red and bromthymol blue, the values pH 6.0–7.6 are common to both bromthymol blue and phenol red, etc. It is therefore usually possible to make a test on any given sample with two different indicators and thus check results. This is one of the outstanding advantages of using several indicators to cover a wide pH range instead of a single wide range indicator, such as the so-called universal or utility indicators. With the single test wide range indicator there is no way of checking results and marked errors may be made with no means of detecting them.

### MIXED AND UNIVERSAL INDICATORS

A mixture of two indicators is often used to obtain color changes at pH values not available from single indicators. The following table lists some of the more commonly used indicator-pairs.

<i>Indicator-pair</i>	<i>Solvent</i>	<i>pH</i>	<i>Color Change</i>
$\frac{1}{2}$ dimethyl yellow, $\frac{1}{2}$ methylene blue...	Alcohol	3.2	Blue violet-green
methyl orange, $\frac{3}{5}$ xylene cyanole FF...	50% Alcohol	3.9	Red violet-green
methyl yellow, $\frac{1}{6}$ methylene blue....	Alcohol	3.9	Pink-yellow green
methyl orange, $\frac{3}{5}$ indigocarmine....	Water	4.1	Violet-yellow green
bromcresol green, $\frac{1}{6}$ methyl orange...	Water	4.3	Orange- dark green
methyl red, $\frac{1}{3}$ methylene blue.....	Alcohol	5.2	Red violet-green
bromcresol green, $\frac{2}{5}$ methyl red.....	Alcohol	5.1	Wine red-green
bromcresol green, $\frac{1}{2}$ chlorphenol red..	Water	6.1	Yellow green-blue violet
bromcresol purple, $\frac{1}{2}$ bromthymol blue	Water	6.7	Yellow-violet blue
neutral red, $\frac{1}{2}$ methyl blue.....	Alcohol	7.0	Violet blue-green
bromthymol blue, $\frac{1}{2}$ phenol red.....	Water	7.5	Yellow-dark violet
cresol red, $\frac{3}{4}$ thymol blue.....	Water	8.3	Yellow-violet
phenolphthalein, $\frac{2}{3}$ methyl green....	Alcohol	8.8	Green-violet
phenolphthalein, $\frac{1}{4}$ thymol blue....	50% Alcohol	9.0	Yellow-violet
phenolphthalein, $\frac{1}{3}$ naphtholphthalein	50% Alcohol	9.6	Pale rose-violet
phenolphthalein, $\frac{1}{5}$ Nile blue.....	Alcohol	10.0	Blue-red
alizarin yellow, $\frac{1}{5}$ Nile blue.....	Alcohol	10.8	Green-red brown

Universal indicators are made by mixing a number of indicators to produce several color changes at different pH values. As might be expected, the result obtained by their use is approximate only, and chiefly of use in preliminary work to be confirmed by further colorimetric or instrumental tests. Two universal indicators in general use are the following:

**Universal Indicator A.**—Solvent: 100 ml. of alcohol. Procedure: dissolve in order 0.06 g. of methyl yellow, 0.04 g. of methyl red, 0.08 g. of bromthymol blue, 0.10 g. of thymol blue and 0.02 g. of phenolphthalein. Titrate with 0.1 *N* NaOH to a yellow color. This indicator has the following series of color values: pH 1 cherry-red, pH 2 rose, pH 3 red-orange, pH 4 orange-red, pH 5 orange, pH 6 yellow, pH 7 yellow-green, pH 8 green, pH 9 blue-green and pH 10 blue.

**Universal Indicator B.**—Solvent: 100 ml. of 50% alcohol. Procedure: dissolve in order 0.0185 g. of methyl red, 0.06 g. of bromthymol blue, and 0.064 g. of phenolphthalein. Titrate with 0.1 *N* NaOH to a green color. The indicator has the following series of color values: pH 1 red, pH 2 red, pH 3 red, pH 4 deep red, pH 5 orange, pH 6 orange-yellow, pH 7 green yellow, pH 8 green, pH 9 green-blue, pH 10 violet, and pH 11 red violet.

### pH TEST PAPERS AND TESTERS

The manufacturers of laboratory supplies offer a wide variety of pH test papers, i.e., strips or rolls of paper impregnated with various indicators. These are available with single indicators for single-range testing, and with more than one indicator for general work. The latter are called wide-range papers when they give a characteristic color for each full pH unit in the range covered, and short-range papers when they give color changes for each 0.5 pH unit. They are available in pH testers or Hydrion Testers, small metal dispensers, each containing a roll of indicator paper and with permanent standard colors for matching on its outer surface. The manufacturers also supply such permanent standards with bottles of universal indicators. The Hellige Simplex Tester has these standards in the form of small color plates so mounted that a glass tube containing the solution to be tested can be placed behind the standards, while an identical glass tube with the same solution is placed behind a series of white plates of the same size as the color plates. In this way compensation can be effected for interfering color or turbidity.

### COLORIMETRIC DETERMINATION OF BUFFERED MATERIALS

One of the most important factors to be considered when the colorimetric method is applied is the degree to which the material being tested is buffered. This is especially important when the pH of colored and turbid materials must be determined. When a highly colored or turbid sample is buffered it can frequently be diluted with distilled water to a point where satisfactory readings can be made with the comparator method without introducing appreciable error. For example, sewage sludges have been accurately tested when a dilution of 1:49 was necessary.<sup>1</sup> The presence of buffer systems in the sludge makes this possible.

In applying the dilution procedure to any substance it is advisable to continue the dilution beyond that required for satisfactory readings so as to determine the point at which marked change starts to take place. This will furnish information on the buffer capacity of the substance being tested. In all cases the distilled water used should be of excellent quality and it should have a pH of 6.4 to 6.8.

It is usually advisable to employ dilution and make the tests on the supernatant liquid after any solids have partially settled. Filtration should be avoided unless it is definitely known that changes in pH will not result. During filtration there may be a gain or loss in carbon dioxide or an action by the filtering medium (paper, glass wool, etc.) which will introduce errors.

<sup>1</sup> McCrumb, Sewage Works Journal, 1, 534, 1929.

## UNBUFFERED OR SLIGHTLY BUFFERED MATERIALS

Some materials encountered in practice are not very highly buffered and a few are unbuffered. In such cases care must be exercised in determining the pH since such solutions are very susceptible to change. Among such materials are most waters, soil extracts, paper extracts, white water, pure sugar liquors, flotation feeds, laundry rinses, clay filtrates, etc.

Distilled water is devoid of buffer action and special precautions must be observed in testing it. Absolutely pure water has pH 7.0 at 25°C. Ordinary distilled water is usually acid, due to absorption of carbon dioxide. Distilled water in equilibrium with the carbon dioxide of the air will have pH 5.7. It may be supersaturated with carbon dioxide to give a pH as low as 5.0. Carbon dioxide may be removed by boiling in Pyrex vessels to give water with a pH of 6.6 to 6.8 but superpure water with pH 7.0 can best be secured by means of a special still. Distilled water should always be kept in Pyrex or tinned vessels and contact with air held at a minimum. In making aqueous solutions or extractions of slightly buffered materials, proportions of material and water should be held constant so that results on different samples will be comparable.

In determining the pH of buffered solutions reasonable differences between the pH of the sample and the indicator solution will not affect the results. However, in the case of unbuffered solutions the pH of the indicator solution must be fairly close to the pH of the sample or the indicator will change the pH (Acree and Fawcett, *Ind. Eng. Chem., Anal. Ed.*, 2, 78, 1930). For this reason the pH of the indicator solution should always be at or near its own midpoint. For example bromcresol green, 4.8, bromthymol blue, 6.8, cresol red, 8.0, etc. This is why it is impossible to secure accurate results on slightly buffered materials when a single wide-range indicator (universal, utility, etc.) is employed. It has been shown that errors as high as 3.0 pH may result (McCrumb, *Ind. Eng. Chem., Anal. Ed.*, 3, 233, 1931). This is because the pH of the wide-range indicator may vary so much from that of the sample.

Where extremely accurate results are desired on unbuffered materials, it may be advisable to use several solutions of the same indicator adjusted to different points on its range, such as bromthymol blue at 6.2, 6.8, 7.4. If the unknown is devoid of buffer action as in the case of distilled water, for example, three values may result such as 6.6, 6.8, and 7.0 respectively. Since the reading 6.8 coincides with the pH of the indicator solution used for that test, the actual pH is 6.8.

All indicator solutions should be adjusted to their respective midpoints and kept in Pyrex bottles sealed with rubber stoppers. Soft glass bottles and cork stoppers should never be used or marked changes in pH may occur. Indicator solutions should not be unduly exposed to the air (poor seals, etc.) since carbon dioxide may lower the pH. In case changes occur the pH can be again adjusted by adding dilute 0.1 *N* acid or alkali as required comparing the indicator solution in a special pair of tubes with the appropriate standard. If, however, buffered solutions are being tested, only gross changes in the pH of indicator solutions need be considered.

In making a pH determination on a slightly buffered solution the indicator solution should be placed in the test tube and the solution being tested run in from a pipet, holding the tip of the pipet near the bottom of the tube. Mixing is then secured by stirring either with the tip of the pipet or with a thin glass rod. Mixing should never be done by placing finger or thumb over the mouth of the tube. The recommended procedure prevents introduction of impurities such as carbon dioxide, etc., and gives accurate results. This is really the only way un-

buffered materials can be tested since electrometric methods are not reliable on very slightly buffered solutions.

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### THE EFFECT OF SALTS

As stated previously, the color of any indicator may be influenced by the actual salt concentration as well as the pH. This effect is commonly known as the "salt error."

By varying the concentration of a buffer mixture and determining the pH both by a hydrogen electrode and the colorimetric method it will be found that absolute agreement occurs only at the concentration of buffer employed in making the standard. Above this concentration the colorimetric method will give results that are slightly higher than those secured by the hydrogen electrode and below this concentration the colorimetric results will be slightly lower. This is illustrated by the results given in the following table.

Effect of Varying the Concentration of a Buffer Mixture

Molar Conc.	Hydrogen Electrode pH	Colorimetric pH	Difference
			pH Hyd. Elect.-pH Color.
0.200	6.33	6.40	-0.07
0.100	6.42	6.45	-0.03
0.050	6.50	6.50	0.00
0.020	6.57	6.55	+0.02
0.010	6.62	6.55	+0.07
0.005	6.68	6.55	+0.13

It will be noted that absolute agreement occurs only at a molar concentration of 0.050, the one employed in making the color standards. Of course none of the differences are pronounced.

The effect of sodium chloride is shown by the data in the following table secured by adding variable amounts of sodium chloride to a phosphate buffer mixture having the same concentration as was employed in the preparation of the color standards.

Effect of Sodium Chloride

Sodium Chloride Molar Conc.	Hydrogen Electrode pH	Colorimetric pH	Difference
			pH Hyd. Elect.-pH Color.
0.00	6.40	6.40	0.00
0.05	6.25	6.40	-0.15
0.10	6.23	6.40	-0.17
0.20	6.15	6.35	-0.20
0.50	6.00	6.25	-0.25
1.00	5.90	6.15	-0.25

Similar data secured by adding magnesium chloride to the same phosphate buffer mixture show the influence of a divalent salt.

Effect of Magnesium Chloride

Magnesium Chloride Molar Conc.	Hydrogen Electrode pH	Colorimetric pH	Difference
			pH Hyd. Elect.-pH Color.
0.00	6.40	6.40	0.00
0.05	5.70	5.90	-0.20
0.10	5.40	5.80	-0.40
0.20	5.20	5.65	-0.45
0.50	4.70	5.26	-0.56

In both instances the pH is reduced, the reduction caused by magnesium chloride being greater than that of the sodium chloride. The salt effect on the hydrogen electrode is greater than on the colorimetric pH.

The indicators used in making the colorimetric measurements given in the three tables above were bromthymol blue, chlorphenol red, *p*-nitrophenol, and bromcresol green.

Additional information on salt effect can be secured by consulting Clark,<sup>2</sup> Kolthoff,<sup>3</sup> Guntelberg and Schiodt,<sup>4</sup> Sendroy and Hastings,<sup>5</sup> McCrumb and Kenny,<sup>6</sup> and Blum and Bekkedahl.<sup>7</sup> The last paper deals exclusively with nickel electroplating and electrotyping solutions.

The investigations of Guntelberg and Schiodt and Hastings and Sendroy would indicate that in the case of the indicators bromphenol blue, bromcresol green, bromcresol purple and phenol red, when the effects of salts are correlated with ionic strengths, salts of different valence types show at the same ionic strengths approximately like effects on the apparent dissociation constants of the indicators.

The ionic strength of a solution is obtained by multiplying the concentration of each ion by the square of that ion's valence number, summing these products and dividing by two. In general the buffer solutions used as standards in the colorimetric method have ionic strengths of 0.05 to 0.1.

In the majority of cases the differences encountered in industrial practice may have little significance. The correction can be determined and applied for each case but frequently it can be disregarded. For example in the case of a nickel plating bath it may make little difference to the plater whether the bath is controlled at pH 5.8 colorimetrically or 5.4 electrometrically. However, to avoid confusion when comparing procedures, the method employed should be given.

<sup>2</sup> Clark, The Determination of Hydrogen Ions, 1928, Williams and Wilkins.

<sup>3</sup> Kolthoff, The Colorimetric and Potentiometric Determination of pH, 1931, John Wiley and Sons, Inc.

<sup>4</sup> Guntelberg and Schiodt, Z. Physik. Chem., 135, 393, 1928.

<sup>5</sup> Sendroy and Hastings, J. Biol. Chem., 82, 200, 1929.

<sup>6</sup> McCrumb and Kenny, J. Soc. Chem. Ind., 49, 425T, 427T, 1930.

<sup>7</sup> Blum and Bekkedahl, Trans. Electro Chem. Soc., 56, 291, 1929.

## THE EFFECT OF PROTEINS

Systematic calibration when proteins are encountered will prove to be much more difficult than in the case of salts. Salts are at least substances of a definite nature, whereas the term protein is used in a very loose manner. For this reason so-called "protein errors" of indicators should never be applied unless it is known definitely that these variations were determined on solutions that are practically identical with the one being tested.

For example, many "protein errors" have been determined on materials like beef broth or some type of bacteriological media. On many of these materials the proteins have undergone considerable hydrolysis, or they are rather dilute. Anyone taking the variations so determined and using them in the measurement of the pH, of say gelatin or casein, might quickly get into trouble.

The following table shows some variations encountered on a 1% solution of gelatin to which variable amounts of sulfuric acid and sodium hydroxide had been added. The gelatin was ash free with a pH of 4.80 (isoelectric). Sulfuric acid was used because this acid is most likely to be encountered in practice.

Effect of Gelatin

Hydrogen Electrode pH	Colorimetric pH	Difference	Indicator
		pH Hyd. Elect.-pH Color.	
2.48	2.40	0.08	Meta cresol purple
2.79	3.20	-0.41	Benzo yellow
3.19	3.55	-0.36	Benzo yellow
3.51	3.85	-0.34	Bromcresol green
3.65	4.00	-0.35	Bromcresol green
3.88	4.20	-0.32	Bromcresol green
4.47	4.60	-0.13	Bromcresol green
4.80	4.85	-0.05	Bromcresol green
5.07	5.00	0.07	Bromcresol green
6.16	6.20	-0.04	Chlorphenol red
6.59	6.65	-0.06	Bromthymol blue
6.80	7.20	-0.40	Phenol red
7.39	7.90	-0.51	Phenol red—Cresol red
7.78	8.50	-0.72	Thymol blue

It will be noted that the differences encountered near the isoelectric point are insignificant being within the sensitivity of the colorimetric method employed. When hydrochloric acid is used the differences are greater in the acid range.

The variations between pH measurements by the hydrogen electrode and the colorimetric method in the precipitation of casein by hydrochloric acid have been determined by Clark and others<sup>8</sup> using methyl red; and by Benton<sup>9</sup> using bromcresol green.

<sup>8</sup> Clark, Zoller, Dahlberg and Weimar, Ind. Eng. Chem., 12, 1163, 1920.

<sup>9</sup> Benton, Ind. Eng. Chem., 20, 15, 1928.

## EFFECT OF TEMPERATURE

Since the pH of a solution depends on the degree of ionization of its constituents and this may be affected by temperature, the influence of temperature on pH is an important factor. Irrespective of the method of measurement employed determinations must be made at a fixed temperature. In the majority of cases a temperature of 25°C. is the most satisfactory although variations in temperature from 20 to 30°C. are usually insignificant for practical purposes.

Certain buffer systems are more sensitive to temperature variations than others. This is particularly true of the borate and carbonate series. Solutions that depend on a carbonate equilibrium are always susceptible to changes in temperature.

In the case of nickel solutions not only does the pH change with temperature but the color of the solution itself may change. Consequently the blanks used in the comparator method should be at the same temperature as the sample to which indicator has been added.

The sulfonphthalein indicators are not influenced by temperature changes to a marked degree but methyl orange and indicators resembling methyl orange are very susceptible to such changes. The indicators LaMotte Yellow, Hellige Orange and Benzo Yellow belong to this class.

## SPECIFIC EFFECTS

In the case of certain sulfonphthaleins the shade of color depends on concentration and depth of layer. Dichromatism is most noticeable in practice with such indicators as bromphenol blue and bromcresol purple. The transmitted light in such cases is primarily red and blue and the ratio of red and blue will vary with the depth of layer. In testing turbid solutions much of the light is reflected by the particles and this gives the same effect as a thin layer of liquid and this tends to modify the color. In such cases it is advisable to substitute another indicator.

Off-color, while not exactly common to all indicators may occur in the case of most two-color indicators under certain conditions. Suspensions, emulsions, and solutions of a colloidal nature may cause this difficulty. Concentrated solutions of such salts as zinc chloride and sulfate frequently give off colors with the sulfonphthaleins. Sometimes on standing a precipitate, presumably of basic salts, will settle out and the colors then secured on the supernatant liquid may then correspond with the color standards. In such cases the original solution may appear clear to the eye, but it must contain dispersed solids which cause the off-color of the indicator. When dealing with such solutions the nitrophenols may be used. When tubes and standards are observed through a blue glass satisfactory color distinctions can usually be secured.

The nitrophenols ordinarily employed for this purpose are 2,4-dinitrophenol (Alpha) (pH 2.6-4.0), 2,5-dinitrophenol (Gamma) (pH 4.0-5.8), *p*-nitrophenol (pH 5.6-7.6) and *m*-nitrophenol (pH 7.2-8.8). The color changes are all from practically colorless to varying shades of yellow.

For further details Michaelis and Gyemant<sup>10</sup> should be consulted.

Difficulty is sometimes encountered in testing soap solutions. In fairly dilute solutions the results may be in good agreement with the hydrogen electrode but certain indicators tend to give low results as the concentration of soap is increased. This is particularly true of thymol blue.

Some indicators are apparently influenced by certain ions in some way not as

<sup>10</sup> Michaelis and Gyemant, *Biochem. Z.*, 109, 165, 1920 (see Clark, *The Determination of Hydrogen Ions*, 1928, p. 128).

yet explainable. Alizarine Yellow G (pH 10.0-12.0), Alizarine Yellow R (pH 10.0-12.0), nitro yellow (pH 10.0-11.6) tend to give high results in the presence of calcium salts.

Michaelis<sup>11</sup> has demonstrated the precipitation of bromthymol blue in a solution of quinine hydrochloride.

However, not all the sulfonphthaleins are precipitated by quinine as Michaelis appears to think. Chlorphenol red gives satisfactory readings in such cases. None of the nitrophenols are precipitated by quinine. Precipitation of bromthymol blue also takes place in solutions used as local anaesthetics in dentistry.

There are a few rare instances in which bromthymol blue gives results that are slightly lower than those found by other sulfonphthaleins. This has been pointed out by Sharp and McInerney<sup>12</sup> in the testing of milk.

Similar results are sometimes encountered in testing concentrated solutions of sulfonated oils.

### EFFECT OF CHLORINE

The action of chlorine must sometimes be taken into consideration in water treatment plants, paper mills, textile mills, etc., whenever the dosage of chlorine is high enough to affect the indicators. When such action occurs the results secured are influenced by the particular indicators in use, the concentration of indicator employed, the buffer capacity of the solution being tested, the temperature and, of course, the concentration of available chlorine.

In the procedure employed with the Slide Comparator (Fig. 14-3) the danger point with the sulfonphthaleins is about 2.0 parts per million of active chlorine. Whenever lower concentrations of indicator are employed as in Nessler tubes, etc., the action of chlorine may cause errors at lower concentrations of chlorine.

There appears to be two types of reaction, chlorination and oxidation. In the case of chlorphenol red and phenol red chlorination appears to predominate at first and the chlorinated dyes which result have lower pH ranges than the original dyes. This results in an increase in the alkaline color which leads to results that are higher than they should be. Of course on longer standing if the concentration of chlorine is high enough fading will occur due to destruction of the dye by oxidation. In the case of the other sulfonphthalein dyes the action is largely destructive and the readings tend to be low or off colors are secured.

The nitrophenols are more stable in the presence of active chlorine and can sometimes be used when the concentration of chlorine is as high as 200 parts per million.<sup>13</sup>

One disadvantage of the nitrophenols should be pointed out here. They are all fairly acidic and their solutions are difficult to stabilize at any definite pH. Consequently they are more liable to give erroneous results in testing unbuffered samples than are the sulfonphthaleins.

### COLORIMETRIC pH EQUIPMENT

Colorimetric pH equipment can be made by the worker if desired using buffer mixtures in test tubes or ampoules but it is more satisfactory to purchase such equipment. Several types are available and the outstanding ones will now be described in some detail. Fuller descriptions can be secured from the manufacturers.

<sup>11</sup> Michaelis, *Practical Physical and Colloid Chemistry*, trans. by Parsons, 1925, p. 41.

<sup>12</sup> Sharp and McInerney, *J. Biol. Chem.*, **70**, 729, 1926.

<sup>13</sup> Lewis and Kukulich, *Paper Trade Journal*, **95**, No. 11, 28, Sept. 15, 1932.



*The Taylor Slide Comparator.*—The Slide Comparator consists of two principal parts, the slide and the base, as shown in Fig. 14-3. The Slide is a Bakelite case 10 inches long,  $2\frac{3}{4}$  inches high and  $\frac{5}{8}$  inch thick. It contains 17 vertical holes and 17 horizontal slots which pass through the exact centers of the holes. In these holes are placed the 9 color standards for any given indicator and 8 ampoules of distilled water. All these ampoules are held in place by a lid which is screwed on the top of the slide.

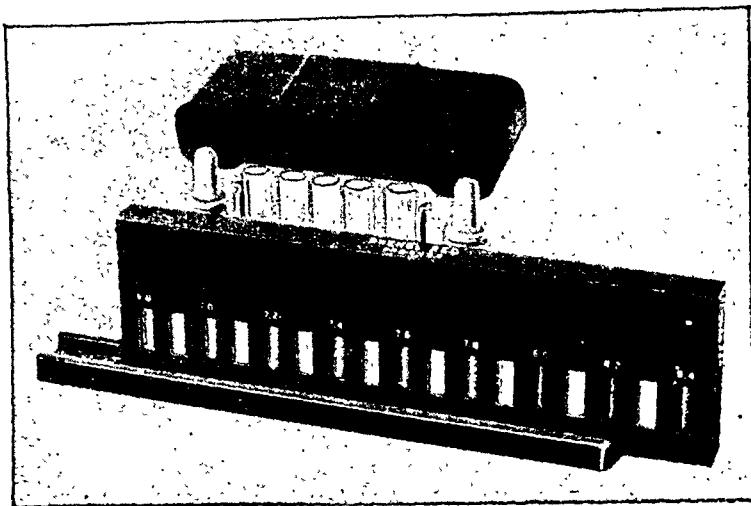


FIG. 14-3. Taylor Slide Comparator.

The base consists of two parts. The lower part contains a slot for the slide fitted with a key to stop the slide at the end standards, two holes containing vials of indicator solution, with 0.5-ml. pipets and nipples, five holes containing test tubes, and a closed compartment for a ground glass plate. Horizontal slots run through the three central holes in the base holding the test tubes, these slots corresponding exactly with any three of the slots in the slide. The upper part of the base serves as a cover for the vials and test tubes when the set is not in use. It is fastened to the lower part by means of spring catches. The complete set, including the slide, is 10 inches long,  $2\frac{3}{8}$  inches wide and 4 inches high, and weighs only 2 pounds.

Making a pH determination consists in only three simple operations.

1. After removing the top of the base, three of the test tubes are placed in the holes back of the slots in the base and filled to the mark (5 ml.) with the sample to be tested. (Fig. 14-4.)
  2. To the central tube 0.5 ml. of the indicator solution is added, by means of the pipet and nipple, and the contents are thoroughly mixed. (Fig. 14-5.)
  3. The slide containing the color standards is now placed in position on the base and, holding the instrument toward a window or other source of daylight, the slide is moved back and forth in front of the test samples until a color match is obtained. The pH is then read off directly from the values on the front of the slide. (Fig. 14-6.)
- Since all color standard slides are interchangeable, that is they can be used with one base, the range of a single slide Comparator can be increased by purchasing additional slides and a supply of the corresponding indicator solutions, with

pipets and nipples. For ranges longer than that of one indicator, however, the Long Range and Dalite Slide Comparators are recommended.

All color standards provided for the various models of slide comparators are guaranteed to retain their accuracy for a period of five years.

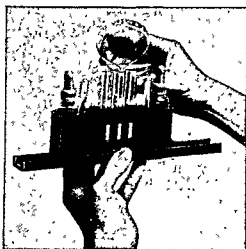


FIG. 14-4.

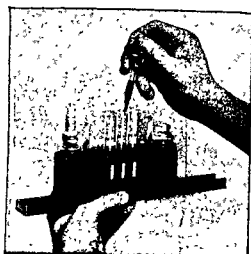


FIG. 14-5.

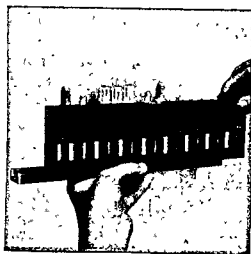


FIG. 14-6.

*The Long Range Slide Comparator.*—This set is designed to meet the needs of workers who require a portable set covering a wider range. It is made in seven models covering the range of any 3, 4, 5, 6, 7, 8, or 9 indicators respectively between the limits pH 0.2 and pH 13.6. It is flexible since its range can be increased simply by securing additional color standard slides. See Fig. 14-7.

Each Long Range Slide Comparator contains one complete Slide Comparator; 2 to 7 extra color standard slides; vials of the corresponding indicator solutions, with 0.5-ml. pipets and nipples; and fourteen 5-ml. test tubes. All models are contained in a polished wooden case 11½ inches long, 9 inches high and 5¾ inches wide, with a handle for carrying. All equipment necessary for making tests is contained in the case so that these sets can be used in field, laboratory or plant.

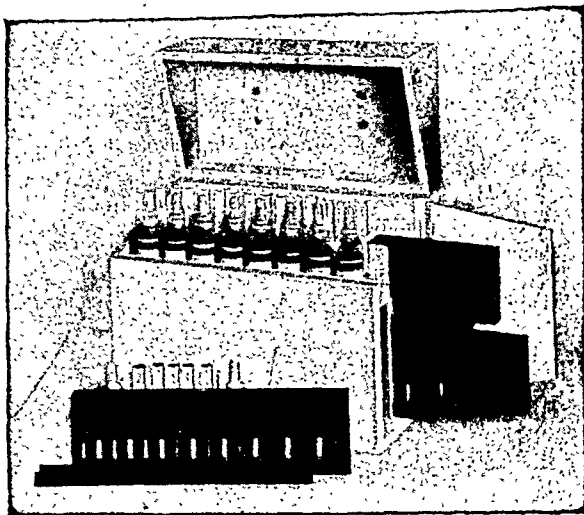


FIG. 14-7. Long Range Slide Comparator.

The total weight of the set varies from  $7\frac{1}{2}$  lbs. to  $9\frac{1}{2}$  lbs. depending on the number of slides.

The method for making determinations is exactly the same as that described for the single Slide Comparator.

**Dalite Slide Comparator.**—In many cases it is necessary to make pH determinations at night. Also in many plants even during the day time the light is not suitable for this type of work. The use of ordinary electric light bulbs and even the so-called dalite bulbs is not satisfactory. The Dalite Slide Comparator, Fig. 14-8,

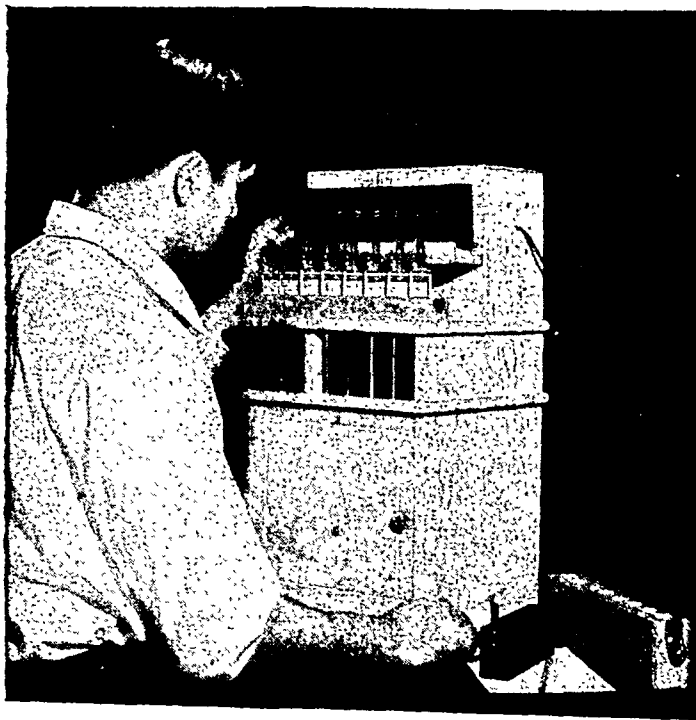


FIG. 14-8. Dalite Slide Comparator.

enables the worker not only to make determinations at night with just as great accuracy as during the day but also assures him that measurements made at night will check those made on the same materials by ordinary daylight.

The set is made in 6 models to cover the range of any 3, 4, 5, 6, 7 or 8 indicators respectively between the limits of pH 0.2 and pH 13.6 in intervals of 0.2 pH. The set is flexible since its range can be increased simply by purchasing additional color standard slides and vials of the corresponding indicator solution.

The pH equipment supplied with this set consists of one complete Slide Comparator; any 2 to 7 additional color standard slides; vials of the corresponding indicator solutions with pipets and nipples; and ten 5-ml. test tubes. Each slide contains 9 color standards for any given indicator and these slides fit in slots in the front of the case as shown in the illustration. Each vial of indicator solution is placed directly above the corresponding color standard slide, thus eliminating error due to the use of the wrong indicator solutions. A top protects the vials when the set is not in use.

The comparator base is supported by a shelf on the front of the box. Directly behind the slots in the base is a piece of Dalite glass and in the compartment behind this is a special 25-watt electric light bulb, with cord, switch, and socket. In the lower part of the box is a cupboard of sufficient size to hold four 1000-ml. Pyrex bottles. This cupboard serves not only as storage for stock bottles of indicator solution but also to bring the comparator to a convenient height for making readings. A rack on the inside of the door holds ten 5-ml. test tubes. A test tube brush is also supplied with the set.

In making determinations three of the 5-ml. test tubes are filled to the mark with the solution to be tested, the proper color standard slide is placed on the base and 0.5 ml. of the corresponding indicator solution is added to the middle tube by means of the pipet and nipple. The light is then turned on and the slide is moved back and forth until a match is obtained with one of the color standards. The pH value is then read off directly from the values on the slide.

**The Roulette Comparator.**—The Roulette Comparator consists essentially of a stationary base and metal band, and a wooden drum which revolves inside the metal band, on ball bearings. A block, which contains three slots, and which is drilled to hold three graduated test tubes, is fastened to the front of the metal band. A 40-watt lamp is fixed in the center of the base and is connected with a standard plug by means of a lamp cord, a piece of Dalite glass is placed in the back of the block between the three test tubes and the color standards, and a piece of etched glass is placed in a slot in the block directly in front of the three test tubes. The block also serves as a visor to cut out light from the outside. With this arrangement the observer always makes his readings under standard, diffused daylight conditions. See Fig. 14-9.

Any three sets of color standards such as chlorphenol red (pH 4.8–6.4), bromthymol blue (pH 6.0–7.6) and phenol red (pH 6.8–8.0) and 24 ampoules of distilled water, are supplied with the set. An extra polished wooden case, containing 50-ml. bottles of the corresponding indicator solutions, 1 empty 50-ml. bottle, four 0.5-ml. pipets with nipples, and 18 marked test tubes, is included as part of the equipment. A fabricoid cover is provided for the comparator.

The revolving drum contains three separate sets of holes, each set being designed to hold 9 color standards and 8 ampoules of distilled water. The color

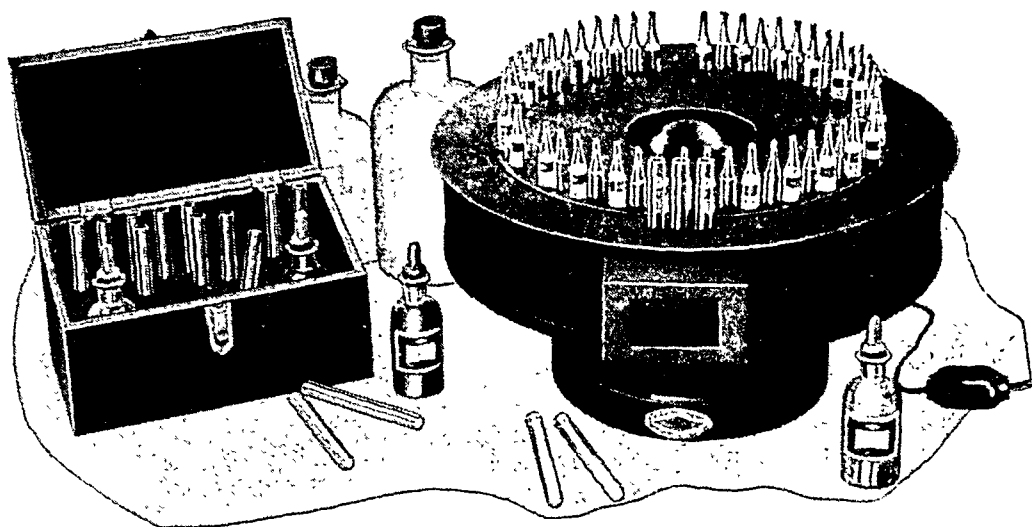


FIG. 14-9. LaMotte Roulette Comparator.

standards are placed in position in order alternating with the ampoules of distilled water. To make a determination three test tubes are filled with the solution to be tested and placed in the three holes in the block. Then 0.5 ml. of indicator solution is added to the middle tube and mixed thoroughly. The light is turned on and the drum revolved until the appropriate standards are behind the test sample. The standards are then shifted by turning the drum until the color through the middle tube exactly matches that of one of the standards on either side of it or lies between them. The pH value is then read off directly from the color standards as the labels on the standards project above the top of the drum. In making a reading the drum must be turned so that an ampoule of distilled water is always directly behind the central test tube.

There is only room for three sets of color standards. Consequently, if the pH of the samples falls outside of the range of these three indicators, another set must be substituted for one of the sets present.

The individual color standards are contained in ampoules approximately 125 mm. long having an outside diameter of 15 mm. The test tubes are made to match the standards and are graduated at 10 ml. The color standards are guaranteed for one year.

**The Hellige Comparator.**—The Hellige Comparator (standard model), Fig. 14-10, consists of a Bakelite housing with hinged front and rear covers and a dustproof enclosed prism for bringing the color fields into juxtaposition. Two acid-proof cemented cells with plane and parallel walls are provided. One cell is to receive the unknown solution with indicator, the other to receive the test solution without indicator. This arrangement provides for color comparison with colored or turbid liquids as well as clear solutions.

In addition to the prism and cells the comparator is supplied with four round measuring tubes with graduations from 5 to 10 ml. in 1/1 ml. for measuring the test solution, 1 pipet with graduations 0.20, 0.25, 0.5 and 1.0 ml. for measuring the indicator solution, 1 opal glass plate, 50 ml. of indicator solution and 1 color disc.

Each color disc consists of a molded resin circular frame with a number (usually 9) of colored glass standards each one representing 0.2 pH so arranged that they can be revolved in the comparator. The color glass standards are made from variable layers of colored glass held together to simulate the colors resulting when

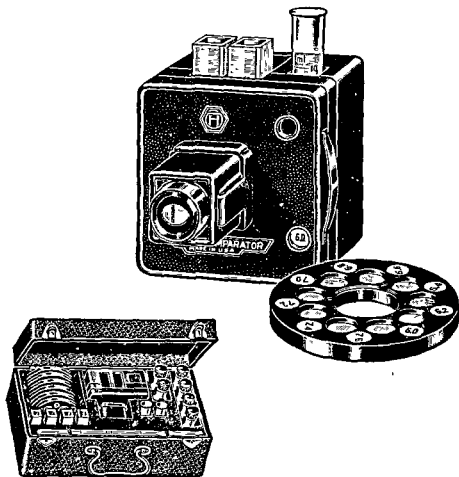


FIG. 14 10 Helge Comparator.

buffer solutions of known pH are treated with the respective indicator. The value of each standard is placed on the disc so that it is visible in a special opening when that particular standard is in the reading position. Only one color standard is visible at a time. Separate color discs are provided for the various indicators.

An illuminator with stand can also be secured to provide the proper artificial illumination.

## Chapter 15

# ELECTROMETRIC HYDROGEN ION MEASUREMENTS

Based on earlier contribution

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Electrometric hydrogen ion (pH) measurements are made with a suitable electrode system as the detecting unit and a potentiometer, or a direct-reading pH meter as the measuring units. The electrodes develop a potential (e.m.f.) proportional to the pH of the solution being measured. The potentiometer and pH meter measure e.m.f. and are discussed in that order.

### POTENTIOMETERS

In order to determine the pH from the difference in potential of two electrodes, the voltage must be measured without allowing any appreciable current of electricity to flow from the cell, for with current flowing the voltage changes, owing to polarization effects at the electrodes. For this reason the measurement cannot be made with a voltmeter, because current is required to actuate such an instrument. The potentiometer is an ideal instrument for measuring voltage with no current flowing from the source. To show how this instrument operates, a brief explanation of the potentiometer principle is given here.

The slidewire  $MN$ , Fig. 15-1, represents an electrical conductor of uniform resistance, along which is placed a scale graduated in uniform divisions. The battery  $B$  causes a steady flow of electricity in this conductor. This is called the working current. The magnitude of this current can be changed by adjusting the rheostat  $R$ . With current flowing from  $M$  to  $N$ ,  $M$  is positive with respect to any point  $O$  between  $M$  and  $N$ . Since the resistance is uniform, the fall of potential is uniform per unit length.

If  $EE_1$  represents the cell for pH measurements the calomel electrode is the positive pole, which is connected to  $M$  through the galvanometer  $G$ . This puts

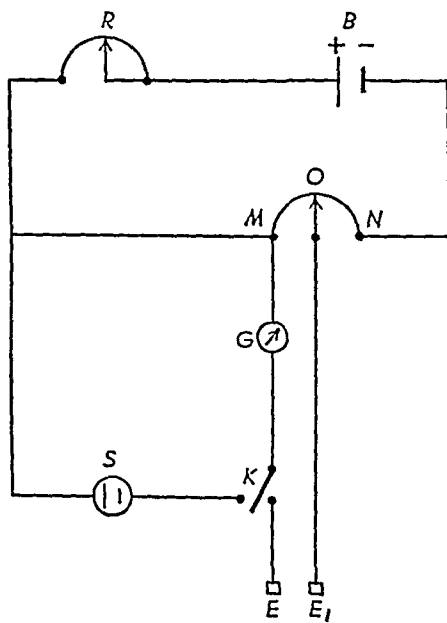


FIG. 15-1.

like polarities in opposition. By adjusting the position of  $O$  the potential difference between  $M$  and  $O$  can be made exactly equal to that between  $E$  and  $E_1$ . When the voltages are balanced the deflection of the galvanometer is zero, and since this is a current indicating instrument, it proves that no current is flowing between the electrodes. Then if the fall of potential between  $M$  and  $O$  is known, the voltage of  $EE$  is measured without any flow of current from the electrodes.

The fall of potential between  $M$  and  $O$  is determined when there is a known potential difference between  $M$  and  $N$ . This is established by replacing the pH measuring electrodes with a standard cell  $S$ , by means of the switch  $K$ . If the voltage of the standard cell is, for example, 1.018 volts, the scale on  $MN$  is graduated in 1018 uniform divisions, and the current is adjusted by means of the rheostat  $R$  until the galvanometer shows no deflection. The potential difference between  $M$  and  $N$  is then 1.018 volts, and the fall of potential for each scale division is .001 volt, or 1 millivolt. If the pH cell is now substituted for the standard cell, the potential difference between the electrodes will be shown directly in millivolts by the number of scale divisions between  $M$  and  $O$  when they are adjusted for voltage balance.

The accuracy of the measurement depends upon the standard cell voltage and the uniformity of the slidewire ( $MN$ ) resistance. Since this uniformity can be determined with practically any desired precision, the accuracy of measurement depends principally on the constancy of the standard cell voltage, and the method is therefore a primary method.

Potentiometers are available with various voltage ranges and accuracies, some designed for portable use. Tables or equations for converting voltage readings to pH values for all electrodes at various temperatures are obtainable. Some forms of potentiometers are calibrated directly in pH, means being provided to correct for solution temperatures.

In addition to the well-known standard types of potentiometers, there are various types of vacuum tube potentiometers. These have been designed primarily for use with the high resistance glass electrode circuits. The resistances involved are too high to permit of the use of any except high sensitivity galvanometers, and only then with the low resistance glass electrode (2-6 megohms). Due to the high resistances involved it is necessary that precautions be taken for properly shielding the potentiometer circuit. This is provided for in most of the commercially available instruments.

It is well to distinguish between accuracy and sensitivity. It is possible to have high sensitivity and low accuracy, and on the other hand to have conditions which would give high accuracy, if there were sufficient sensitivity. The sensitivity depends principally on the galvanometer used. If, with an arrangement not capable of very accurate results, a very sensitive galvanometer were used, its indications would be misleading if the sensitivity were not distinguished clearly from accuracy.

The most important factors affecting accuracy of results are the accuracy of the measuring instrument used, the character of the solutions being measured and the electrodes used, and the accuracy with which the reference electrode potential is known.

### DIRECT-READING pH METERS

The negative-feedback principle is widely used in the design of direct-reading pH meters. Fig. 15-2 shows the important features of such a circuit. The glass electrode is connected to the grid of an electrometer tube  $T_1$ . This increases the



negative potential of the grid and so reduces the current through  $T_1$ . Therefore the voltage drop across the plate resistance of this tube,  $r_p$ , decreases and the voltage at the plate increases. Since this plate is connected to the grid of  $T_2$ , the voltage increase is imposed on this grid of  $T_2$ , the second stage in the amplifier. After the third stage, the voltage increase at the cathode of the output tube is registered on the meter  $A$ . A converse sequence of events occurs if the negative potential of the grid of  $T_1$  is decreased.

The overall effect is that the voltage change across the meter will show an increase or decrease in value as the plate voltage at  $T_1$  changes. Current then

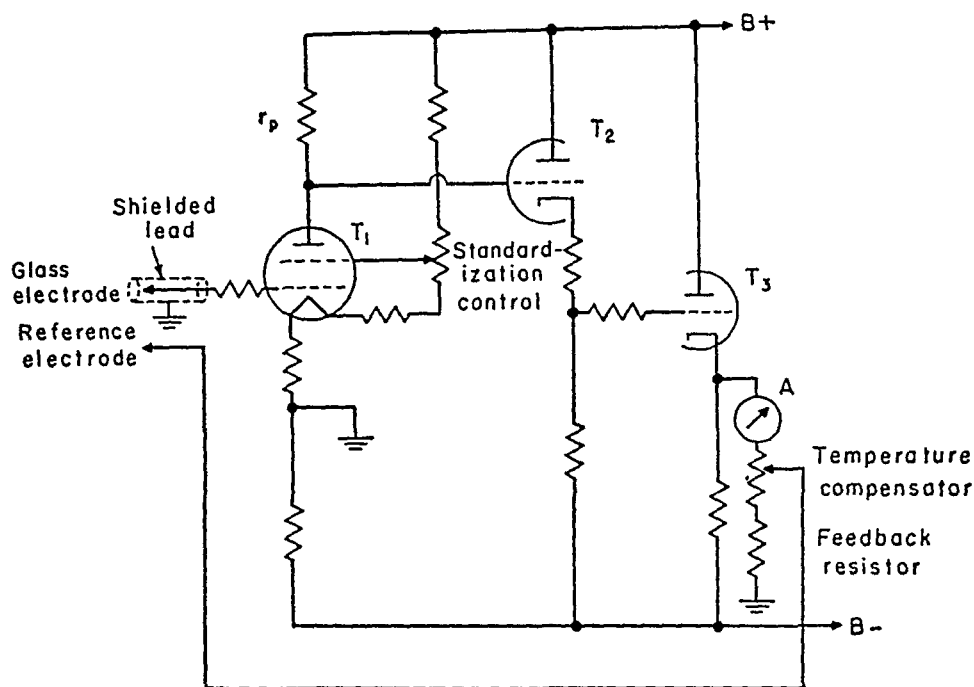


FIG. 15-2.

passes through the meter and the feedback resistor to the circuit ground. The voltage developed across the feedback resistor is applied to the reference electrode through a Temperature Adjust rheostat or other type of temperature compensation. The feedback voltage is opposite in polarity to the voltage signal from the glass and reference electrodes. When the voltage across the feedback resistor reaches a value equal to the voltage signal between the glass and reference electrodes, a steady current is maintained in the output circuit and the meter indication is directly proportional to the signal voltage.

A direct-reading instrument has few manipulative steps, and is adaptable to continuous recording or control of industrial operations or processes. Temperature compensation can be provided by causing the feedback current to flow through a temperature-sensitive resistor located in the input circuit to supply the balancing voltage. If this resistor is placed in the solution to be measured, temperature compensation can be achieved automatically. pH measurements can be made within  $\pm 0.1$  pH unit. When buffer standardizations are made, the meter needle is set to the pH of the buffer by the standardization control knob. This control also compensates for electrode asymmetry potential and instrument drift.

## ELECTRODE SYSTEMS

A single electrode is not sufficient for pH measurements because there is no convenient method for measuring its potential, but the potential of two electrodes, the absolute potential of one of which is known and is unaffected by pH, can be compared. It is therefore customary to use a fixed electrode as a reference, and to use as a measuring electrode one best suited to the measurement at hand.

For those who are not familiar with the theory relating e.m.f. of electrodes and pH, the reader is referred to the treatise on hydrogen-ion measurements by Britton, *Hydrogen Ions*, D. Van Nostrand Company, 1956.

**Reference Electrodes. Calomel Electrode.**

—The calomel electrode is almost universally used as a reference electrode, due to its constancy of potential and ease of preparation. The calomel electrode is one in which mercury and calomel are in contact with a definite concentration of potassium chloride. These are contained in a vessel which may vary in design according to conditions of use. Two common types of calomel electrode are shown in Fig. 15-3; (a) is a commercial type with fiber contact, (b) is the same except for the ground-glass joint.

The potential of the mercury with respect to that of the solution depends on the concentration of mercurous ions from the calomel, but this is governed by that of chloride ions, which are produced in the solution by potassium chloride as well as by calomel. The proportion of the total number of chloride ions that is due to the potassium chloride varies with the KCl concentration. The voltage of the calomel electrode therefore depends on the concentration of potassium chloride in the electrode solution. Saturated, normal and tenth normal solutions are used.

The saturated calomel electrode is used more generally than either of the others. It is more easily prepared, and has some particular advantages.

Special precaution must be taken to prevent diffusion between the saturated solution of a salt bridge with the less concentrated solutions of the normal and tenth normal electrodes, whereas with the saturated electrode there is no tendency toward diffusion. When diffusion is prevented the potentials of the normal and tenth normal electrodes are fairly stable at room temperatures, but at higher temperatures it is difficult to prevent diffusion, with its resulting error in potential. The saturated electrode shows no change in potential between 5° and 60°C., other than that due to temperature. The temperature coefficient is approximately 0.8 millivolt per degree C. Another advantage of the saturated calomel electrode is that its conductivity is high, which makes for increased sensitivity.

An objection to the saturated electrode is that the solution may creep over the edge of the containing vessel with the resulting formation of masses of crystals.

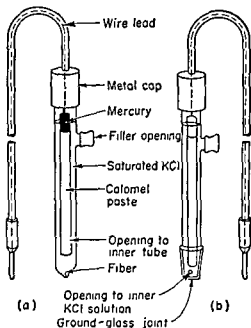


FIG. 15-3. Reference Electrodes. (a) Commercial type with fiber contact; (b) Same, but with ground-glass joint.

This is avoided in the design shown in Fig. 15-4, if the electrode is immersed in a container of distilled water when not in use.

For accurate and reliable potentials, extremely pure chemicals must be used in calomel electrodes. Mercury specially purified and calomel produced by electrolysis for the purpose can be commercially obtained in appropriate quantities, and their use is recommended. Chemically pure potassium chloride dissolved in distilled water is a suitable solution for use with them.

The saturated electrode is easily prepared. For a saturated KCl solution put the salt into warm distilled water in a beaker and stir it thoroughly with repeated addition until no more of it will dissolve. Then stir in enough calomel to saturate the solution. A small quantity is sufficient as it is not very soluble. When the solution is cooled to room temperature, it should contain undissolved potassium chloride and calomel. Prepare enough solution to fill a reservoir for flushing the electrode from time to time. Add sufficient mercury (amount depends upon construction of electrode) to make contact with the platinum terminal, and sufficient calomel ( $\text{Hg}_2\text{Cl}_2$ ) to assure saturation, an excess is advisable. Moisten with saturated KCl solution, shake vigorously, and then nearly fill with saturated KCl solution. If the electrode is not of the self-flushing type, care must be exercised in flushing the salt bridge occasionally.

**Silver Chloride Electrode.**—Comparable in principle to the calomel electrode is the silver-silver chloride electrode. It has largely been used in studies on activities of chlorides in solution, but has also received attention as a reference in pH measurements. This electrode is not as readily prepared as is the calomel electrode, but it is highly reproducible, stable over extended periods of time, and has a small temperature coefficient.

The potential of the silver-silver chloride electrode depends upon the method of preparing the silver and the chloride. Methods have been described by Brown,<sup>1</sup> Harned,<sup>2</sup> McInnes,<sup>3</sup> Noyes and others.<sup>4</sup>

**Measuring Electrodes.**—The glass electrode is by far the most widely used measuring electrode, especially for analytical control work. However, the others have various, though more limited applications, and the hydrogen electrode is the ultimate standard. Therefore the various types require description.

**Hydrogen Electrode.**—The hydrogen electrode consists of a noble metal coated with platinum black, immersed in the solution and under a definite partial pressure of hydrogen gas. Such an electrode is illustrated in Fig. 15-5. Means are provided for introducing the hydrogen gas, and allowing the gas to escape without forcing the solution entirely away from the metal.

Electrodes with large surfaces are generally not advisable as they are more difficult to saturate with hydrogen and therefore come to equilibrium less quickly.

In work with ordinary chemical solutions, and when high accuracy is not essential, the solution being measured may be contained in an open vessel, but the



FIG. 15-4.

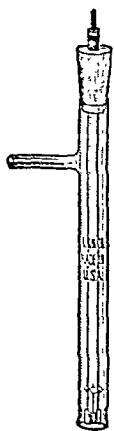


FIG. 15-5.

<sup>1</sup> J. Am. Chem. Soc., 56, 646, 1934.

<sup>2</sup> J. Am. Chem. Soc., 55, 4849, 1933.

<sup>3</sup> J. Am. Chem. Soc., 37, 1445, 1915.

<sup>4</sup> J. Am. Chem. Soc., 39, 2532, 1917.

electrode potential will be slightly influenced by oxygen absorbed from the air. For precise work the vessel should be stoppered with provisions for carrying the electrodes through the stopper, and for allowing the gas to escape.

An electrode is said to be in equilibrium when its potential remains constant if the solution does not vary. The potential of the hydrogen electrode is not constant until the platinized surface is saturated with hydrogen, and any reducing action due to hydrogen is completed.

*Limitations.*—In some solutions, notably biological fluids, the platinum black may become clogged with substances which prevent absorption of hydrogen. The hydrogen electrode cannot be used in solutions containing strong oxidants like ferric ion, dichromates, nitric acid, peroxides, and chlorine, nor in those containing strong reductants, such as sulfurous acid ( $\text{SO}_2$ ) and hydrogen sulfide. Some organic compounds are very susceptible to reduction, particularly those of the aromatic series, such as azobenzene, aniline dyes and some unsaturated acids. In a solution containing either oxidizing or reducing compounds, a noticeable drift in the voltage occurs and a balance is difficult to obtain. The oxidizing or reducing action must be completed before the voltage is steady. The measurement is not trustworthy, for the pH value of the solution may be seriously changed in such reactions.

The hydrogen electrode cannot be successfully applied to solutions containing metal ions that fall below hydrogen in the electromotive series of metals and, also lead, all of which are reduced on the platinum electrode.

*Platinizing the Electrodes.*—The film of platinum black is deposited by electrolysis in 3% platonic chloride solution containing 0.025% lead acetate. The electrode should be thoroughly cleaned before platinizing. Using two dry cells in series it usually requires from 30 seconds to 1 minute to deposit the platinum black. Experience will determine the amount of plating necessary. The electrodes should be washed with distilled water, and immersed in distilled water when not in use. The electrodes should not be allowed to dry thoroughly.

*Hydrogen Gas.*—A very convenient source of hydrogen is the compressed gas supplied commercially in metal cylinders. A cylinder containing 100 or 200 cubic feet is commonly used in the laboratory, while small cylinders are available for portable use.

Compressed hydrogen produced by electrolysis may be sufficiently pure to use directly from the cylinder for measurements of ordinary accuracy, but it is common practice to pass it through solutions of potassium hydroxide and pyrogallol and then through water to remove traces of oxygen and other impurities that would affect the potential of the hydrogen electrode.

*Quinhydrone Electrode.*—Some of the difficulties encountered in the use of the hydrogen electrode are avoided by using a quinhydrone electrode. The basis of this electrode is a piece of platinum or gold the same as used for the hydrogen electrode, but the surface of the metal is not platinized and it is not supplied with gaseous hydrogen. Instead, a small quantity of quinhydrone (benzoquinhydrone) is dissolved in the solution, and in certain conditions the electrode in the solution acquires a potential that is definitely related to the hydrogen-ion concentration of the solution. The potential is measured against that of a calomel electrode, and the pH value is found from the measured voltage in the same manner as with a hydrogen electrode.

Billmann<sup>5</sup> was the first to describe the quinhydrone electrode for the pH

<sup>5</sup> Ann. Chim. Phys., 15, 109, 1921.

measurements. Morgan, Lammert and Campbell<sup>6</sup> have published a series of papers covering detailed studies of this electrode. The quinhydrone electrode is quickly prepared, develops its potential rapidly and is not readily poisoned.

Rather than describe the method of preparing quinhydrone, it is suggested that this material be obtained from chemical manufacturers or suppliers of high grade chemicals.

Although the quinhydrone electrode can be applied successfully to many solutions containing oxidizing and reducing substances in which the hydrogen electrode would give erroneous results, still it is not applicable in all cases. Measurements have been made with it on dilute nitric acid solutions, unsaturated organic acids, and on a variety of oxidizing systems that are of too low an oxidizing intensity to disturb the electrode potential.

*Limitations.*—The quinhydrone electrode is not applicable over the entire pH range. In the acid range, pH 0 to 7, it is excellent. In alkaline solutions strongly buffered, results of fair accuracy can be obtained to about pH 9.0. In solutions poorly buffered, the upper limit is approximately pH 8.0. In the latter case it is essential not to add an excess of quinhydrone, because it reacts with the alkali and changes the pH value of the solution. About 6 to 8 drops of a saturated solution of quinhydrone in acetone is sufficient for 50 ml. of test solution.

If the pH value of a solution measured with a hydrogen electrode differs from that with a quinhydrone electrode, the difference may be due to the "salt error" in the quinhydrone value. The hydrogen electrode is assumed to have no salt error. The magnitude and sign of the salt error (positive or negative divergence from the correct pH value) of the quinhydrone electrode depends upon the type and concentrations of the salts present in the solution. The salt error in nickel plating solutions of total salt concentration about 2.0 *N* is below +0.05 pH. In a 10.0 *N* ammonium sulfate solution it is approximately -0.2 pH, while in a 4.0 *N* sodium chloride solution it is approximately +0.2 pH. Since most solutions are far more dilute than these, the salt error is generally negligible.

In high purity (99%) sugar solutions the quinhydrone electrode gives values which are approximately 0.2 pH low, while on low purity products, such as molasses, the values are high. Over purity ranges of 80% to 97% the quinhydrone electrode gives good results.

*Antimony Electrode.*—Of the various metal and metal oxide electrodes that have been described, the antimony electrode has proved to be the most satisfactory. It does not require gas or a catalytic surface as does the hydrogen electrode; it does not require the addition of a reagent as does the quinhydrone electrode. The antimony electrode is not readily prepared, but once made up is useable for very extended periods. It may be obtained commercially ready for use. It is a rugged electrode and in certain designs is used industrially for continuous plant service. The inherent accuracy of the antimony electrode is not as great as is the hydrogen or the quinhydrone electrode.

*Limitations.*—These have been described by Perley.<sup>7</sup> Notable among them is that the e.m.f.-pH relation varies with the degree of buffering of the solution, and that the degree of saturation with air, particularly below pH 7, affects the potential-pH relationship. The antimony electrode is not applicable to solutions which are oxidizing or are strongly reducing, nor in solutions containing more than a

<sup>6</sup> J. Am. Chem. Soc., 53, 2154, 1931 and 54, 910, 1932.

<sup>7</sup> Trans. Am. Inst. Chem. Engrs., 29, 1933.

trace of copper, silver, or other metals below antimony in the electrochemical series of the elements. However, under known conditions this electrode serves a very useful purpose in measuring pH over the range of pH 3 to 12. It is being used quite extensively in sugar solutions (beet, raw cane, and refinery), paper mills, water treatment, pigments, etc. For measurements on a given sample extending over long periods of time, this electrode is particularly suitable.

**Glass Electrode.**—The work Hughes,<sup>8</sup> Kerridge,<sup>9</sup> McInnis and Dole,<sup>10, 11</sup> and others have shown the possibilities of the glass electrode. A typical glass electrode is shown in Fig. 15-6. The shell of the electrode consists of a small bulb or tip of

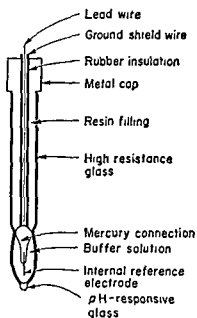


FIG. 15-6. Glass Electrode.

special glass sealed to a stem for ordinary Pyrex glass. In this manner the hydrogen ion response is confined entirely to the area of the special glass membrane, eliminating any variance caused by the depth of immersion so long as the tip of the electrode is completely wetted by the solution. Inside the bulb is a dilute hydrochloric acid solution, and dipping into this is an internal reference electrode, which is generally either a silver-silver chloride electrode or a calomel electrode. The inner cell is tightly sealed to the atmosphere by means of a wax or plastic dielectric and a metal or plastic cap. The connecting leads are shielded and the shield grounded to the measuring circuit. The glass electrode assembly is dipped into the solution under examination together with an external reference electrode. Owing to the very high resistance of the glass, 10 to 100 megohms, the e.m.f. of the assembly must be measured with special vacuum tube voltmeters.

Many glass compositions have been investigated for their pH response. The soda-lime type commonly used, Corning 015, is the eutectic of the ternary system  $\text{SiO}_2\text{-CaO-Na}_2\text{O}$ , and is composed of 72.2 mole per cent  $\text{SiO}_2$ , 6.4 mole per cent  $\text{CaO}$ , and 21.4 mole per cent  $\text{Na}_2\text{O}$ . This glass has the desirable properties of low melting point, high hygroscopicity, and relatively high electrical conductivity. These factors, plus durability at high temperatures and high alkalinities, resistance to abrasion and pressure when pressed onto surfaces, as well as whether the pH response is linear, must be considered in the fabrication of a glass electrode.

General purpose glass electrodes are characterized by relatively low electrical resistance, permitting construction of glass tips so thick that they are practically unbreakable. The pH response of these electrodes follows a linear relation very well between pH 1 and pH 11. In more alkaline solutions the observed values of pH are too small and must be corrected from nomographs supplied by the manufacturer. The error at a given pH increases with increase of the concentration of alkali metal ions, especially sodium ion. Above pH 12 these corrections become so large that even with corrections an accurate pH value cannot be obtained.

<sup>8</sup> J. Am. Chem. Soc., 44, 2860, 1922.

<sup>9</sup> Biochem. J., 19, 611, 1935.

<sup>10</sup> Ind. Eng. Chem., Anal. Ed., 1, 57, 1929.

<sup>11</sup> J. Am. Chem. Soc., 53, 3315, 1931.

The sodium error at high pH can be reduced considerably by substituting lithium, or lithium plus a little cesium or rubidium, for sodium in the composition of the glass. One glass with small sodium error at high pH is composed of 65 mole per cent  $\text{SiO}_2$ , 28 mole per cent  $\text{Li}_2\text{O}$ , 3 mole per cent  $\text{Cs}_2\text{O}$ , and 4 mole per cent  $\text{La}_2\text{O}_3$ . Barium oxide may be substituted for cesium and lanthanum. Small amounts of the larger-size barium, cesium, or lanthanum ions apparently diminish the sodium error by their blocking action. The small sodium ions are less able to find the opening sufficiently large for their migration from one hole to another in the glass membrane or into the glass-solution interface.<sup>12</sup> Lithium glass electrodes are generally used in the pH 9 to 14 range because of their lower sodium ion errors in high alkaline solutions. Special types of glass electrodes are available for high-temperature measurements over the entire pH range. Even in highly alkaline solutions at the boiling point some of these electrodes will show only 0.2 pH deviation at pH 13.7 in 1 M sodium hydroxide. These types should be standardized with buffer solutions in the high pH range when used in alkaline solutions.

Since the mechanism of the glass electrode involves no electron exchange, it is the only hydrogen-ion electrode not disturbed by oxidizing or reducing agents. The glass electrode does not affect the solution under examination. This permits poorly buffered solutions and those containing volatile components or suspended matter to be measured.

Commercial glass electrodes are made in many forms for special applications (Fig. 15-7). Some electrodes require only a volume of one drop, although generally a volume of 5 ml. is required to cover completely the sensitive portion of the glass bulb.

*Limitations.*—In solutions of proteins and other colloids that tend to adhere to the sensitive membrane, the glass electrode may yield erroneous results. It cannot be used in an acid fluoride solution. Only special types will withstand prolonged use at 100°C. and in strongly alkaline solutions. Difficulty may be encountered when the glass electrode is used in nonaqueous media, due to partial dehydration of the glass membrane.

*Measurements with the Glass Electrode.*—The first step is standardization of the instrument. This is done by immersing the glass and calomel electrodes into a buffer of known pH, setting the meter scale or needle to the pH of the buffer, and adjusting the proper controls to bring the amplifier circuit into balance. The pH of the standard should be within one, or at the most two, units of the pH of the sample to be measured. For highest accuracy the instrument should be standardized at one pH and checked against a second standard buffer so that the two buffers bracket the pH of the test sample. If measurements are made within 2 pH units of the buffer value, a 10°C. temperature variation will result in an error of less than 0.07 pH.

A glass electrode exhibits a very fast response to rapid and wide changes of pH in buffered solutions. However, valid readings are obtained more slowly in poorly buffered or unbuffered solutions, particularly when changing to these from buffered solutions, as after standardization. The electrodes should be thoroughly washed with distilled water after each measurement and then rinsed with several portions of the next test solution before making the final reading. Poorly buffered solutions should be vigorously stirred during measurement; otherwise the thin

<sup>12</sup> Perley, G. A., *Anal. Chem.*, 21, 391, 394, 559, 1949.

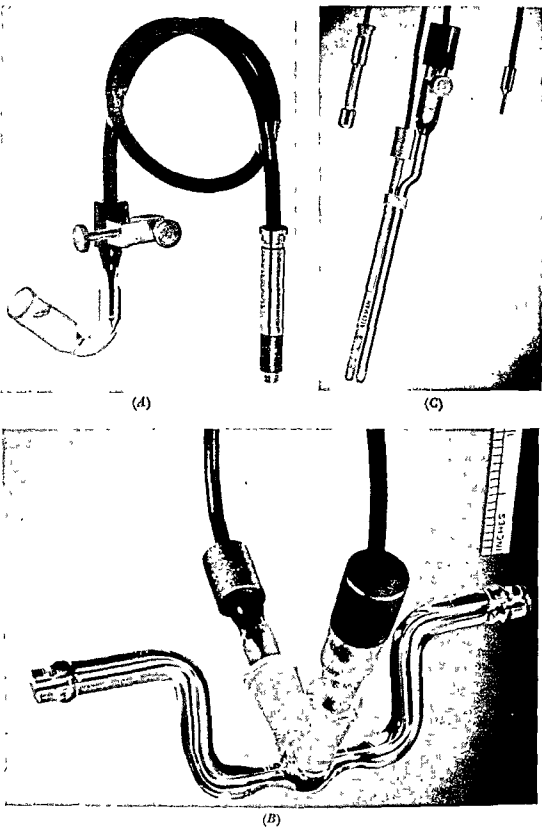


FIG. 15-7. Special Styles of Glass Electrodes.  
*A* = One drop assembly; *B* = Flow assembly; *C* = Probe assembly.



layer of solution at the glass solution interface tends towards the composition of the particular kind of pH-responsive glass.

The glass electrode should not be allowed to become dry, except during long periods of inactivity. However, it will return to its responsive condition when immersed in water for several hours prior to use. Electrodes constructed from special glass are available for continuous use at temperatures not exceeding 85°C. and for intermittent use up to 100°C. Glass electrodes of special construction are also available for operation under pressure conditions. A special reference electrode must be employed at elevated temperatures and under pressures above atmospheric. Only a silver-silver chloride reference electrode performs satisfactorily.

## Chapter 16

# STATISTICAL INTERPRETATIONS

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### PRECISION OF ANALYTICAL DETERMINATIONS

The analytical chemist is concerned, first of all, with the reproducibility of his results. If the results of duplicate determinations do not check each other, it is hopeless to expect them to check a known value. Lack of reproducibility means that some condition affecting the result is not being adequately controlled. Analytical chemists have long been aware that it is easy to be misled on the question of reproducibility. If one solution is prepared for a colorimetric determination by dissolving a sample and following a sequence of steps preparatory to using the colorimeter, there is only *one* determination. Aliquots from this one solution will reveal only the performance of the instrument and will tell nothing about the differences that might be found between *two* solutions prepared from separate portions of the sample. The trap here is perfectly apparent. However, many chemists overlook the fact that *two* or more determinations, run in parallel on the same bench, on the same day, using the same reagents, etc., will almost certainly give a misleadingly optimistic impression of the real reproducibility of the procedure. Every analytical chemist should carefully specify the circumstances under which he expects any claimed reproducibility to be actually attained. If these circumstances refer to the agreement between results obtained in two or more laboratories on the same sample, the experienced analyst will recognize that this is a much more severe test of the procedure than would be parallel determinations on the same bench.

Experience has shown that the within-laboratory precision is, for all practical purposes, very much the same for different laboratories. The results from several laboratories differ because there are individual laboratory peculiarities, such as reagents, the environment, and the interpretation of the procedure, that are temporarily constant for each laboratory. In different laboratories the reagents may differ in source and in age. The temperature, humidity, and light will be different, and the analysts may differ in the way in which they follow the instructions. These circumstances affect the determinations made within a laboratory in the same way and, therefore, do not disturb the agreement of duplicate results within a laboratory. The presence of such temporarily constant errors is demonstrated by the frequent lack of agreement shown by the results from several laboratories. It is, therefore, not surprising that the agreement among laboratories falls short of the agreement among results within any one laboratory.

Very often, for research studies within one organization, the within-laboratory agreement is the appropriate measure of the analytical errors. The *comparison* of different samples, for example, is largely free from constant errors, whatever their source. This follows because, in taking a difference, constant errors drop out. Even here, attention must be paid to the circumstances. If a study is made of changes in the composition of a material stored for an extended period of time, the analytical error may approach that applicable for comparisons between laboratories. Over an extended time period, reagents will be replaced, analysts may change, and seasonal changes may occur. None of these sources of error will be revealed by duplicate determinations conducted in parallel. The analytical chemist must always bear in mind the use to be made of the analytical results, because the analytical error depends to a considerable extent upon the circumstances involved.

It is common to say that precision refers to the agreement of duplicate results and that accuracy refers to the error as measured from the true value. There is a suitable precision for every set of circumstances under which comparisons are made. There is always a local, more or less permanent, set of circumstances that introduces a systematic departure from the true value. Analytical chemists are engaged in devising analytical procedures and in carefully specifying them so that these systematic errors are kept small. Only then do results from different places show acceptable agreement. An analytical procedure should not be vulnerable to small departures from the conditions prescribed for making the determinations. At the very least, small departures from the procedures that are likely to occur in practice should be explored.

Suppose, for example, that the volume of reagent, the time and temperature of digestion, the concentration and temperature of the washing solution are among the specified conditions for conducting the analysis. Besides determinations conducted strictly according to specification, some determinations should be made changing each condition in turn by a small amount. The results should also be independent of moderate changes in environment or sources of reagent, and these should be investigated. Of course, if the procedure specifically indicates the importance of holding particular conditions within certain close limits, these limits must be respected. The spread of the results of determinations in which such minor departures have been purposely introduced will be a much more realistic appraisal of the checks that can be expected when different laboratories use the procedure. Let  $x_1, x_2, \dots, x_n$  be  $n$  individual results where  $n$  individual minor departures from the procedure have been tried. The estimate,  $s$ , of the standard deviation,  $\sigma$ , is given by

$$s = \sqrt{\frac{\sum x^2 - (\sum x)^2/n}{n - 1}}.$$

Of course, if any of the results are obviously apart from the group, this departure from the procedure should be followed up. It may be necessary to include a warning for the conditions responsible. Such results should be omitted from the calculation of the standard deviation.

The use of the precision as estimated from parallel runs is justified only when the determinations to be compared have also been carried out either in parallel, or under as favorable circumstances as those that existed for the runs used for estimating the precision. Very often a considerable number of materials have been run in duplicate. These duplicates can be used to estimate the precision.

If duplicate results are available on each of  $n$  materials, the  $n$  differences,  $d_1, d_2, \dots, d_n$ , can be used to calculate an estimate,  $s$ , of the standard deviation by substituting in the formula  $s = \sqrt{\Sigma d^2/2n}$ .

The samples should cover a range of amount of the element involved. The individual  $d$ 's should be plotted against the sample averages to reveal if the error depends on the amount present. Sometimes the error is proportional to the amount present. In that event it is useful to express the standard deviation as a percentage of the amount present, the ratio being called the *coefficient of variation*. A quick approximation for the coefficient of variation can be obtained by first converting each difference to a percentage of the average of the duplicates. These percentages,  $p_1, p_2, \dots, p_n$ , may be substituted in the formula,  $C.V. = \sqrt{\Sigma p^2/2n}$ , to estimate the coefficient of variation. It may sometimes suffice to group the materials into two or three classes on the basis of the amount present and to calculate a standard deviation for each class. Fitting a straight line when the analytical error varies with the amount present requires weighting of the data. Textbooks on statistics should be consulted when this problem arises.

In a routine process, the adequacy of the sampling may be ascertained by running one determination on each of two samples from each lot sampled. These results are treated as duplicate results. The standard deviation is calculated as above using the formula for differences. If the standard deviation computed when using individual analyses from duplicate samples is persistently larger than that calculated from duplicates on the same sample, this is evidence that the sampling is contributing to the error.

A good estimate of the standard deviation requires a considerable number of independent measurements. Even with 20 independent errors, the standard deviation may be either underestimated by as much as 25% or overestimated by approximately 50%. For this reason, the accumulation of information from many pairs of duplicates is highly desirable.

## ACCURACY OF ANALYTICAL DETERMINATION

Analytical procedures are tried out in most cases on "known" materials. These may be standard samples, or purified substances, or materials run by some other accepted, and perhaps more tedious, method. Whenever possible, a number of such known materials should be used rather than running a lot of determinations on just one material. Considerably more can be learned from one or two determinations on each of several materials than from the same total number of determinations on just one material.

Suppose there are  $n$  materials available covering a range of amount of the item to be determined. Designate the known values by  $x_1, x_2, \dots, x_n$  and the results of single determinations by  $y_1, y_2, \dots, y_n$ . Prepare a graph using the known values as abscissas and the corresponding results as ordinates. Use the same scale on each axis. The amount found should, in theory, equal the amount taken and the points should lie along a straight line,  $y = x$ , with a unit slope through the origin. If the only errors in the results are random precision errors, the points should be about equally distributed above and below this line. If the points are all, or nearly all, on one side of the 45° line and about the same amount away from the line, there is an indication of the presence of a constant error. In this case a parallel line,  $y = a + x$ , may fit the points satisfactorily, and the intercept,  $a$ , on the  $y$  axis

is an estimate of the constant error. The points may be chiefly on one side but departing more and more from the line with increasing amounts of the item determined. This suggests a type of systematic error that is proportional to the amount present. A line,  $y = bx$ , corresponds to this state of affairs. Sometimes it is necessary to use the general formula,  $y = a + bx$ , to allow for both an intercept and a slope other than unity. In the event that the points depart from a linear relationship and if the method must still be used in spite of this serious handicap, it will be necessary to do considerable work to establish an empirical relationship.

In order to get a reasonable number of points, additional knowns may be obtained by preparing mixtures of known proportions of the available materials. Duplicate determinations should be run on each material. Denote the duplicate values for each material by  $y$  and  $y'$ . There will be two determinations,  $y_i$  and  $y'_i$ , for the material with known composition  $x_i$ . Formulas appropriate for the lines  $y = x$ ,  $y = a + x$ , and  $y = bx$  will be given here. The formulas for the general line,  $y = a + bx$ , are available in many textbooks.

The advantage of fitting a line to a series of points is that the deviations of the points from the line furnish an estimate of the analytical errors in addition to the estimate based upon the differences between the duplicates at any point. In effect, the line is fitted to the averages for the pairs of duplicates. For computational reasons, the formulas are based upon the individual results and not on the averages.

As a first step, obtain the  $n$  differences,  $d_1, d_2, \dots, d_n$ , for the  $n$  pairs of duplicates and calculate  $\Sigma d^2/2$ . The precision is estimated by  $s = \sqrt{\Sigma d^2/2n}$ , and this precision will be compared with an estimate,  $s_a$ , of the analytical error based on the departures of the points from the straight line fitted to the points.

For the line,  $y = x$ , there are no constants to compute. The sum of the squares of the deviations of all  $2n$  points from this line is given by  $\Sigma(y - x)^2 + \Sigma(y' - x)^2$ . Note that each  $x$  is used twice, once with each duplicate. This sum of squares must be diminished by  $\Sigma d^2/2$ , the portion corresponding to the precision error. The remainder,  $R = \Sigma(y - x)^2 + \Sigma(y' - x)^2 - \Sigma d^2/2$ , should be divided by  $n$  and the square root taken to obtain  $s_a$ , the analytical error as revealed by the departure of the points from the ideal line,  $y = x$ . If  $s_a$  is less than  $s$ , this is pure chance and not to be taken seriously. Almost always  $s_a$  will be larger than  $s$ . It is customary to calculate the ratio,  $F = s_a^2/s^2$ , of the two variances in order to form an opinion as to whether the points depart from the line,  $y = x$ , sufficiently to suggest that a line with an intercept or a line with a slope other than unity would provide a better fit. If this ratio exceeds 5.0 for five materials, or 3.4 for eight materials, or 2.7 for 12 materials, the evidence strongly suggests that the amounts found depart from the amounts taken in some systematic manner.

For the line,  $y = a + x$ ,  $a$  is obtained by calculating  $a = (\Sigma y + \Sigma y' - 2\Sigma x)/2n$ . The sum of the squares of the deviations from this line is given by  $\Sigma(y - x)^2 + \Sigma(y' - x)^2 - 2na^2$ . This sum is diminished by  $\Sigma d^2/2$ , and the remainder,  $R_a$ , is divided by  $(n - 1)$  to give a new estimate,  $s_{aa}$ , for the analytical error. The estimate,  $s_{aa}$ , is never larger than the estimate,  $s_a$ , found for the line,  $y = x$ . Generally, it will be considerably smaller. A statistical test is available to determine whether or not the line,  $y = a + x$ , has substantially decreased the sum of the squares of the deviations that was found for the line,  $y = x$ . The decrease,  $(R - R_a)$  is divided by  $(s_{aa})^2$ . This is another  $F$  ratio and if it exceeds 7.7 for five materials, 5.6 for eight materials, or 4.8 for twelve materials, the presence of a constant error is indicated.

The line,  $y = bx$ , may prove a better fit. Calculate  $b = (\Sigma xy + \Sigma xy')/2\Sigma x^2$ . The sum of the squares of the deviation from the line,  $y = bx$ , is given by  $\Sigma y^2 + \Sigma y'^2 - b(\Sigma xy + \Sigma xy')$ . Again this sum is diminished by  $\Sigma d^2/2$ , and the remainder,  $R_b$ , when divided by

$(n - 1)$ , gives another estimate,  $s_{ab}$ , for the analytical error. This estimate is never larger than  $s_a$ , and usually is smaller. The decrease  $(R - R_b)$ , is divided by  $(s_{ab})^2$ , and the same  $F$  test is applied as in the preceding paragraph. A large  $F$  ratio indicates the presence of a systematic error that is proportional to the amount present.

In the two paragraphs above, the estimates of error,  $s_{aa}$  and  $s_{ab}$ , are obtained by taking the square root after dividing the remainder by  $(n - 1)$ .

If the simple line,  $y = x$ , proves inadequate, one or the other of the two lines,  $y = a + x$  or  $y = bx$ , will usually provide a much better fit. The analytical error, as calculated from the deviations of the points from one or the other of these lines, will be reasonably close to the estimate,  $s$ , calculated from the duplicates. This statistical examination is intended to reveal a defect in the procedure and to give a hint of the nature of the defect. If the procedure is used without correcting the defect, the accuracy,  $s_a$ , is given by the deviations from the line,  $y = x$ , and certainly not by the agreement shown by duplicates.

The estimate of the standard deviation that is based on the deviations from the fitted line is usually a more realistic value than that obtained from parallel duplicates. There are often unconscious efforts to bring about agreement between duplicates. The use of different materials avoids this all too common tendency. The determinations for several materials are probably spread over a longer period of time. In fact, it is a good idea to number all the determinations from 1 to  $2n$ . A set of  $2n$  cards should be numbered and shuffled to randomize the order. The determinations should be run in this random order.

### SOME IMPORTANT USES OF THE STANDARD DEVIATION

All the preceding remarks have been directed to making sure that a meaningful estimate of the analytical errors has been obtained. A standard deviation based upon parallel duplicate determinations is appropriate for comparing two materials run simultaneously. Let the average of  $n_1$  determinations on material  $M_1$  be  $m_1$  and the average of  $n_2$  determinations on material  $M_2$  be  $m_2$ , and  $s$  be the estimate of the standard deviation of the analytical procedure. It is assumed that  $s$  is based on other data and with 30 or more degrees of freedom. In practice  $n_1$  and  $n_2$  are likely to be very small and possibly both of them equal to one. The degrees of freedom equal the number of independent errors. The degrees of freedom are equal to  $n$  if  $n$  pairs of duplicates are used to estimate  $s$ , and to  $(n - 1)$  if the estimate is based on  $n$  repeat determinations on one sample.

Compute

$$t = \frac{(m_1 - m_2)}{s} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

If  $t$  exceeds 2.0, there is evidence at the 95% level of confidence for a difference between the materials. If  $s$  is based upon fewer degrees of freedom, the values of  $t$  for various degrees of freedom are shown in Table 16-1.

The analyst may be interested in comparing the average of  $n$  determinations on a material with some specified or claimed value,  $V$ , for the material. If the average  $m$  of  $n$  determinations differs from  $V$ , the analyst cannot dispute the claimed  $V$  unless he believes that the difference  $(V - m)$ , exceeds that which he might have obtained if  $V$  had been the true value. This leads right back to the deviations from the straight line  $y = x$ , and it is the standard deviation,  $s_a$ , based

## TABLE 16-1. SELECTED VALUES OF $t$

Confidence Level, %	Degrees of Freedom = D.F.						
	1	2	4	8	16	32	$\infty$
95	12.7	4.30	2.78	2.31	2.12	2.04	1.96
90	6.3	2.92	2.13	1.86	1.75	1.70	1.64

on these deviations that is appropriate here. It is unreasonable to expect to get any better checks on  $V$  than were obtained on known materials.

Calculate

$$t = \frac{(V - m)\sqrt{n}}{s_a}$$

and apply the same criteria for  $t$  as given above.

Analysts are often expected to set confidence limits about the results they report. Again it is important to select the right standard deviation for any given circumstances. The factor applied to the standard deviation to obtain confidence limits depends on the number of degrees of freedom associated with the estimate of the standard deviation. The confidence limits for a single determination are obtained by multiplying the standard deviation by the appropriate factor,  $t$ , and then adding and subtracting this quantity from the result obtained in the determination. The confidence limits for an *average* of  $k$  determinations are obtained by first dividing  $s$  by the  $\sqrt{k}$ . If  $k$  is small and these are the only determinations available to estimate the standard deviation, then the factor for the confidence limit will be correspondingly large. It is better, whenever possible, to use an estimate of  $s$  based on prior information, i.e., on many degrees of freedom, and to use the appropriate smaller multiplying factor than to rely exclusively on the immediate data. The assumption here is that the immediate results for which confidence limits are desired were obtained under as favorable circumstances as were the determinations used to establish a firm estimate of the appropriate standard deviation.

Suppose an analytical procedure is stated to have a standard deviation,  $\sigma$ , under certain specified circumstances. If an estimate,  $s$ , of the standard deviation based on  $f$  degrees of freedom is available from determinations also made under these circumstances, it is possible to compare the estimate with the claimed value  $\sigma$ . There will, as a rule, be no complaint if the estimate,  $s$ , is smaller than  $\sigma$ . The question really arises when  $s$  is larger than  $\sigma$  and one wishes to know whether it is enough larger to be considered evidence that there is a real difference between  $s$  and  $\sigma$ . A ratio, called chi square, is computed by multiplying the ratio of the two variances by the degrees of freedom.

$$\chi^2 = \frac{s^2}{\sigma^2} f.$$

If  $\chi^2$  exceeds certain values, depending on the number of degrees of freedom, there is evidence for a real difference between the observed and claimed value.

TABLE 16-2. SOME VALUES FOR CHI SQUARE

Confidence Level, %	Degrees of Freedom = <i>f</i>					
	1	2	4	8	16	32
95	3.84	5.99	9.49	15.5	26.3	46.2
90	2.71	4.61	7.78	13.4	23.5	42.6

### ROUNDING DATA

Suppose a chemist obtains the result 11.42 by a procedure that he knows has a standard deviation of 0.05. This means that the result may deviate from the correct value by as much as  $\pm 10$  units in the second decimal place so the chemist promptly rounds the result to 11.4. The meaningless figure has been suppressed, but at a price. There is a correct value, though unknown. Imagine a long series of such rounding of similar determinations. It is a solvable mathematical problem to ascertain the average magnitude for each of the following quantities:

True values minus results to two decimal places.

True values minus results to one decimal place.

These two average "misses" are respectively 0.040 and 0.046. The average miss is increased 15% by rounding even in this apparently justified instance. More vividly, in this instance, the average of four rounded values is no better than the average of three unrounded results. This increase in the departure from the true value is usually not important in any particular result reported, and so rounding is a very general practice. The place where rounding is absolutely reprehensible is in reports of a study of an analytical procedure. These "meaningless," uncertain, terminal figures are just the ones that *do* reveal the random errors in the work. Rounding greatly diminishes the efficiency of estimates of the standard deviation. Naturally, when the data are rounded, the results have the appearance of being in excellent agreement, but the ability to estimate the standard deviation of the procedure is greatly impaired and sometimes altogether removed.

### CONTROL OF ROUTINE ANALYTICAL WORK

In routine work, particularly in maintaining a check on a production process, it is usual to run just one determination per sample. Two problems arise here. One is the possible appearance of a value out of line with the usual values. The other has to do with checking on the laboratory to prevent a gradual deterioration in the quality of the analytical work. The latter problem is customarily dealt with by introducing at irregular intervals some known reference material or by sending



back, under a new number, a sample already reported on. If known samples that are not recognized can be used, the matter is simple and the test has already been described. If samples are reissued, the only evidence available is the agreement shown by the duplicates. The standard deviation for a procedure in routine use should be well established. Let  $\sigma$  denote the standard deviation. Consider what might be expected regarding the differences between duplicates if many pairs of duplicates were available for examination.

10% of the differences will exceed  $2.33 \sigma$   
5% of the differences will exceed  $2.77 \sigma$   
1% of the differences will exceed  $3.64 \sigma$   
0.5% of the differences will exceed  $3.97 \sigma$

The laboratory director must select some appropriate multiple of  $\sigma$  and, when this difference is exceeded, take what action is deemed necessary. If the multiple selected is  $3.64\sigma$ , then there is one chance in a hundred that such a difference could occur in the normal course of events without any deterioration in the work. Too small a factor will lead to frequent unwarranted suspicion of inferior work.

The appearance of a value that is out of line with the usual run of values usually involves the production force as well as the laboratory. The quality control charts in the production area are designed to catch just such values, and the analytical laboratory should be familiar with the appropriate charts. When a result is obtained that the laboratory knows will go outside the control lines on the production control chart, it would seem a wise precaution to check the determination immediately. Production may be inclined to ascribe the undesirable result to poor analytical work and it would be proper to anticipate this action whenever possible.

## Chapter 17

# THE ANALYTICAL USE OF THE MICROSCOPE

By Walter C. McCrone and Louise K. Forlini

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**Introduction.**—Chemical microscopy permits the exact identification of an unknown substance, of an unknown compound, or of a desired component in a heterogeneous sample. Even though it may be present in only trace amounts, the component is identifiable so long as it maintains its identity as a separate phase. Results are obtained in terms of the compounds present rather than the elements, allowing a distinction between isomers, polymorphs, or different combinations of the same ions. Even where orthodox methods of chemical analysis are applicable, the optical method may prove more expeditious.

Microscopical methods, by their nature, require only small amounts of sample. Physical properties such as refractive index, melting point, etc., may be determined on nanogram quantities ( $10^{-9}$  g.), if necessary. The majority of the techniques are nondestructive, allowing recovery of the sample.

## MORPHOLOGY AS THE BASIS FOR IDENTIFICATION

Many materials can be identified at a glance by their morphological characteristics, that is, their external form or shape. The microscopist can identify a surprisingly large number of metals and alloys, bacteria, plant and animal fibers, pure crystalline compounds, animal cells and tissues, diatoms, starch grains, pollen grains, etc. It is, however, necessary for him to be directly familiar with these materials, or to have access to photomicrographic atlases of potential materials. No such complete atlas exists, although a number of small compendia are available.

For example, natural textile and paper fibers possess unique morphological characteristics: scales on wool fibers, nodes on flax, serrated cells in esparto, pitted bag-like cells in nonconiferous wood pulp, etc.

Analysis by morphology is also useful in air pollution studies. Figure 17-1 is a photomicrograph of atmospheric debris collected in dust-fall jars in Chicago, showing cotton and wool fibers, bits of paper and wood, fly ash, soot, a bit of pigeon feather, quartz and other minerals, bits of paint, iron oxide scale, and particles of glass.

In many police laboratories it is common practice to vacuum clean the clothing of an arrested suspect and to examine the sweepings microscopically. Items of forensic interest might be pieces of glass, paint chips, hairs or fibers, pills, clumps

of dirt, metal filings, bits of unburned explosive, etc. It is extremely difficult to be at the scene of a crime without picking up microscopic evidence on the clothing and shoes, while leaving other microscopic particles at the scene. The latter are collected by sticking a transparent adhesive tape on broken windows, window sills, door jambs, blown or wrecked safes, etc.

To increase the sensitivity or ease of morphological analysis, optical properties such as refractive index may have to be measured. The microscopist may have to identify chemical compounds by the addition of a reagent to a test drop of the unknown, comparing any resulting precipitate with a description, drawing, or

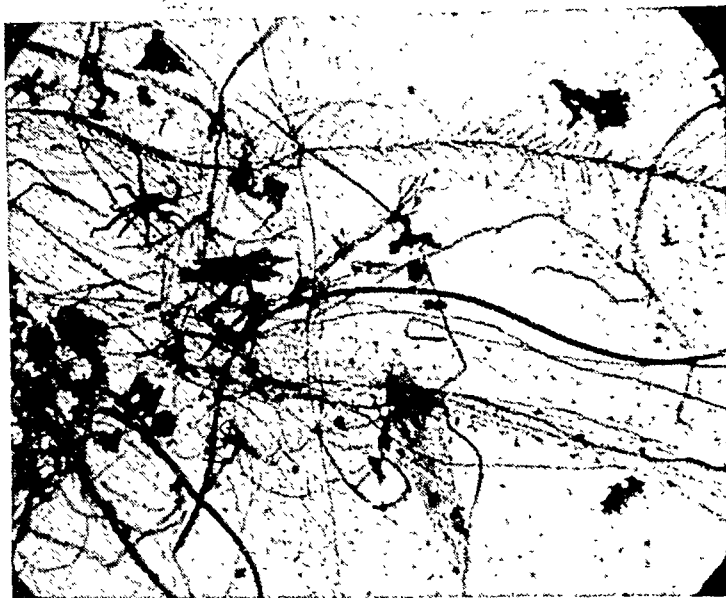


FIG. 17-1. Settled Dust from Chicago Dust-Fall Jar.

photograph of a known precipitate obtained under identical conditions. Fusible compounds may have to be melted and examined for characteristic properties, such as refractive index of the melt.

Measuring a number of significant properties of the compound and comparing them with the descriptive and numerical data available in the literature, the microscopist can then identify an unknown. If a similar item of known source is available for comparison, he can prove identity or nonidentity.

The desired component of a mixture may have to be separated or concentrated by crystallization, fusion, or precipitation, or by staining or "optically isolating" it by immersion in an appropriate refractive index medium.

The usefulness of morphological and optical data in analysis, unfortunately, depends on its availability in a useful form. A number of fiber atlases have been compiled,<sup>1</sup> and tables of crystallographic data are available for all the minerals

<sup>1</sup> Lochte, *Atlas der Menschlichen und Tierischen Haare* (Schops, Leipzig, 1938); von Bergen and Krauss, *Textile Fiber Atlas*, 2nd Ed., Textile Book Publishers, New York, 1949; Luniak, *Identification of Textile Fibres*, Pitman, London, 1953; Matthews, *Textile Fibers*, Ed. Mauersberger, 6th Ed., John Wiley and Sons, Inc., New York, 1954; Wildman, *Microscopy of Animal and Textile Fibers*, Wool Industries Research Association, Leeds, 1954; Carpenter and Leney, *Papermaking Fibers*, State University of New York, Syracuse, 1952; *Identification of Textile Materials*, Textile Institute, Manchester, 1951; *Textile Fibers under the Microscope*, Imperial Chemical Industries Ltd., 1939.



and most of the common inorganic compounds.<sup>2</sup> Certain small groups of organic compounds have also been studied.<sup>3</sup> *Analytical Chemistry* has published crystallographic data on 242 compounds as a monthly feature.<sup>4</sup> Most of the latter descriptions are complete with respect to crystal morphology, crystal optics, X-ray powder data, and unit cell dimensions.

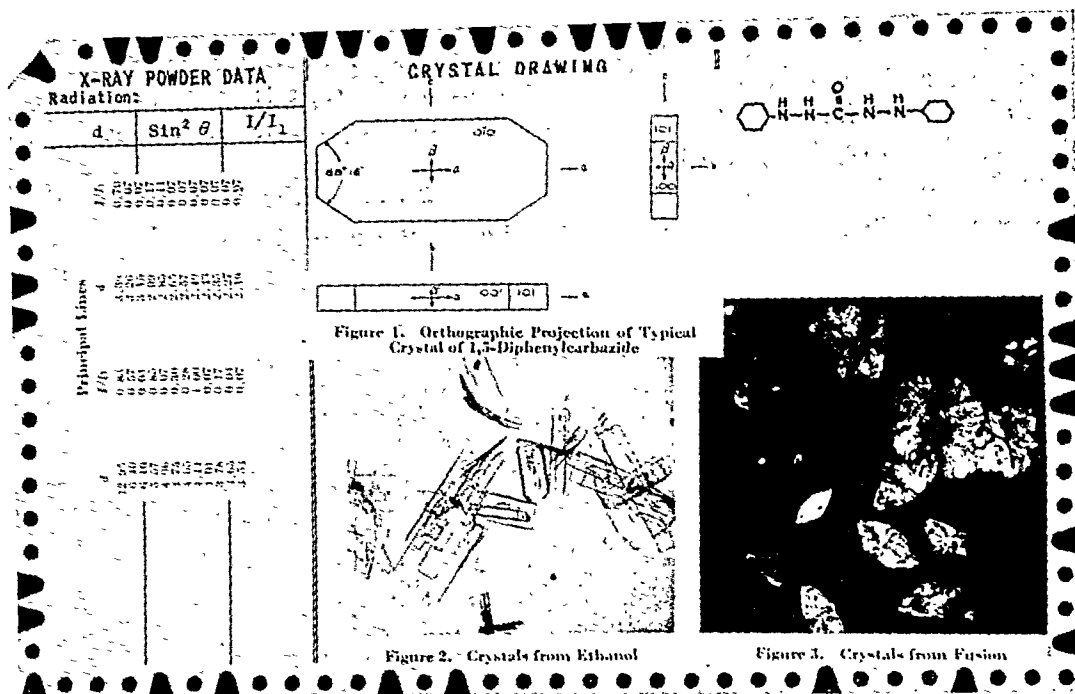


FIG. 17-2c. Back of Card for 1,5-Diphenyl Carbohydrazide.

A punched-card system for tabulating and using crystallographic data has been devised by one of the authors.<sup>5</sup> Each card contains data on the morphological, X-ray, optical, and fusion properties of the compound (Fig. 17-2).

<sup>2</sup> Groth, *Chemische Kristallographie*, 5 Vols., Engelmann, Leipzig, 1906-19; Winchell, *Microscopic Characters of Artificial Minerals*, John Wiley and Sons, Inc., New York, 1931, and *Optical Properties of Organic Compounds*, 2nd Ed., Academic Press, New York, 1954; Donnay and Nowacki, *Crystal Data*, Geological Society of America, New York, 1954; Larsen and Berman, *Tables for the Identification of the Non-Opaque Minerals*, U. S. Geo. Survey Bull. 848, 1934; Porter and Spiller, *The Barker Index of Crystals*, Vol. I, Hefter, Cambridge, 1951, Vol. II, 1956; Palache, Berman, and Frondel, *Dana's System of Mineralogy*, Vol. I, John Wiley and Sons, Inc., New York, 1944, Vol. II, 1951, Vol. III (in preparation); Delfet, *Repertoire des Composés Organiques Polymorphes*, Desoer, Liege, 1942.

<sup>3</sup> Aromatic nitrogen compounds by Bryant, *J. Am. Chem. Soc.*, 65, 130, 1943; amino acids by Keenan, *J. Biol. Chem.*, 62, 163, pharmaceuticals by Keenan, *J. Assoc. Off. Agr. Chem.*, 27, 153, 1944, and Keenan and Eisenberg, *J. Amer. Pharm. Assoc.*, 35, 94, 1946; sugars by Wherry, *J. Am. Chem. Soc.*, 40, 1852, 1918.

<sup>4</sup> During the period March 1948 to June 1961. Now published as a regular feature of *The Crystal Front*, issued quarterly by McCrone Research Institute, Chicago. The data on 230 of the 242 compounds were tabulated in *The Crystal Front*, Vol. I, No. 3, 1959.

<sup>5</sup> McCrone, W. C., *Anal. Chem.*, 28, 972, 1956.

## IDENTIFICATION OF PURE COMPOUNDS

## A. CRYSTAL GEOMETRY

Crystalline materials are usually described morphologically in terms of crystal form, habit, and angles, and, when possible, crystal system.

*Crystal Systems.*—The external faces of a crystal are directly related to the internal arrangement of atoms, the crystal lattice. Unlike the random arrangement found in liquids and noncrystalline materials, the atoms in crystals are arranged in a repeating three-dimensional array. There are six such possible arrangements, constituting the six crystal systems:

The cubic system has an equal spacing of atoms along three mutually perpendicular directions, chosen as the three *a* axes. It has a minimum of four axes of

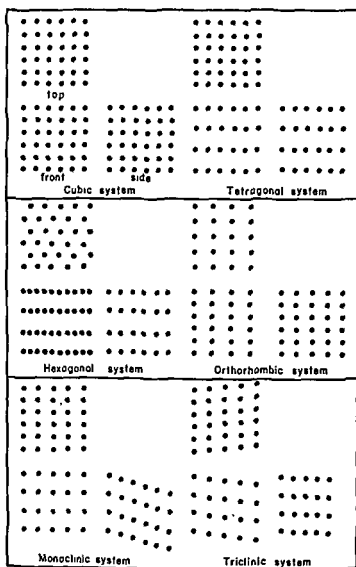


FIG. 17-3. Arrangement of Lattice Points in the 6 Crystal Systems. Reproduced with permission from Kolthoff and Elving, *Treatise on Analytical Chemistry, Part I*, Interscience Publishers, Inc., New York.

threefold symmetry, which form the body diagonals of a cube defined by the three  $a$  axes.

The tetragonal system has equal spacing of atoms along two mutually perpendicular directions, chosen as the two  $a$  axes. Normal to the plane thus formed the spacing is different, and designated the  $c$  axis. It has one fourfold axis of symmetry, the  $c$  axis.

The hexagonal system, which includes both the hexagonal and rhombohedral classes, has equal spacing of atoms along three directions  $120^\circ$  apart in the same plane, the three  $a$  axes. Normal to the plane thus formed the spacing is different ( $c$  axis). The  $c$  axis is a three- or sixfold axis of symmetry.

The orthorhombic system has unequal spacing of atoms along three mutually perpendicular directions. It contains at least two symmetry planes. The axes are chosen on the basis of spacings so that  $c < a < b$  as determined by X-ray diffraction or by interfacial angles.

The monoclinic system has unequal spacing along two mutually oblique directions and normal to the plane thus formed the spacing is also different. At least one plane of symmetry is present. The unique axis perpendicular to the plane of symmetry is  $b$ . The other two axes lie in the plane of symmetry and are chosen so that  $c < a$  and simple forms result.

**The Triclinic System.**—Crystals of this system have unequal spacing of atoms along three mutually oblique directions. Three prominent directions are chosen such that  $c < a < b$  and simple forms result. No symmetry need be present (Fig. 17-3).

**Miller Indices.**—The notations usually used for naming the crystal faces are the *Miller Indices*, which express the intercepts of each face on the axes, in the order  $a$ ,  $b$ ,  $c$ . The crystal is oriented so that  $a$  lies front (+) to back (−),  $b$  lies right (+) to left (−), and  $c$  lies top (+) to bottom (−) (Fig. 17-4). Thus 111 indicates a pyramid face, and 001 a face perpendicular to the  $c$  axis (Fig. 17-5).

**Forms.**—Similar external faces are classified as *forms*, for example, the six faces of a cube are all similar and constitute the cube form (Fig. 17-6). Two parallel faces having no equivalents are called a pinakoid; 3, 4, 6, 8, or 12 similar parallel faces form a prism, if they intersect at a point they form a pyramid. More than one type of form is usually required to complete a crystal.

**Habit.**—This is the general shape of a crystal, or the particular combination of faces developed (Fig. 17-7). It depends on the environment during growth (solvent, impurities, temperature, etc.) as well as the "nature of the beast."

**Constancy of Interfacial Angles.**—Both ideal and distorted crystals of the same substance have identical *crystal angles*. In any distortion, the general shape of the crystal may be changed, but not the crystal angles (Fig. 17-8). This is an expression of the law of *Constancy of Interfacial Angles*. The crystal angles of most use microscopically are the so-called profile angles, observed when the crystal lies on a face. A cube shows  $90^\circ$  profile angles; an octahedron,  $60^\circ$  or  $120^\circ$  angles. Crystal angles can be measured with the microscope using a graduated rotating stage and a cross-hair eyepiece. Stage and crystal are centered, and readings are taken with each side of the angle parallel to one of the crosshairs.

**Rational Indices.**—Crystal forms and habits are also governed by the law of *Rational Indices*, which states that the ratios of the intercepts of different crystal

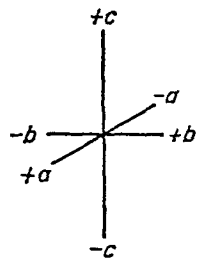


FIG. 17-4. Crystallographic Axes in the Orthorhombic System.

faces on the different crystallographic axes are in the ratios of small integers. The axial ratios are best determined by X-ray diffraction, and expressed as  $a:c$  for the tetragonal and hexagonal systems, and  $a:b:c$  for orthorhombic, monoclinic, and triclinic systems. Ammonium dihydrogen phosphate, a tetragonal crystal, has an axial ratio  $a:c = 1:1.002$ ; the distance between atoms along the  $c$  axis is 1.002 times the spacing between atoms along the  $a$  axis. The interfacial angle can be

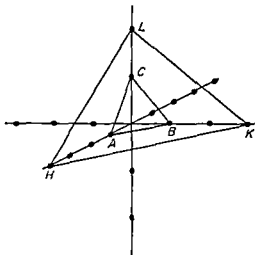


Fig. 17-5. Miller Indices: Face  $ABC = 111$ , Face  $HKL = \bar{3}46$ . Reproduced with permission from Kolthoff and Elving, *Treatise on Analytical Chemistry*, Part I, Interscience Publishers, Inc., New York.

The crystal systems of the modifications are usually different. Two of the most common examples are carbon, crystallizing as the cubic diamond and the hexagonal graphite, and the tetragonal (red) and orthorhombic (yellow) forms of mercuric iodide.

**Cleavage.**—Crystals may show a tendency to break along certain definite planes, parallel to faces or possible faces. Nearly perfect *cleavage* is exhibited by limestone (calcite), since it breaks up into well-formed rhombohedra on grinding.

### OPTICAL PROPERTIES

The spacing of atoms determines not only the system, shape, and angles of a crystal, but its optical properties as well. A chemical or petrographic microscope is essential for the study of optical crystallography. It must possess polarizer and analyzer Nicol prisms (or polarizing films), a graduated centerable revolving stage, cross-hair eyepieces, compensators, and a good condenser.

**Refractive Index.**—The most important optical property is the refractive index, which can be visualized as the degree of slowing of light as it passes through a substance. Elements of higher atomic weight are more effective in slowing light, so that compounds containing the heavier atoms usually have higher refractive indices, as shown in Table 17-1. The refractive index is constant for a substance of definite composition. It is influenced, however, by the wavelength of illumination used, and the temperature of the sample.

calculated from the axial ratio trigonometrically. If the tangent of one-half the angle about  $c$  is  $1/1.002 = 0.998$ , then the angle about  $c$  is  $2(44.94^\circ) = 89.88^\circ$ .

**Twinning.**—Crystals are often *twinned*. In most cases, twinning results in formation of re-entrant angles as in the examples shown (Fig. 17-9). Randomly intergrown crystals are not twins; the term is limited to situations where two or more interpenetrating crystals bear a definite, unique, and characteristic angular relationship. The common composition plane, or twin plane, will always coincide with a possible crystallographic face. The different portions of the twinned crystal can be differentiated by optical tests.

**Polymorphism.**—A compound showing *polymorphism* can crystallize with different internal lattices, thereby giving correspondingly different external crystal morphology and internal physical properties.



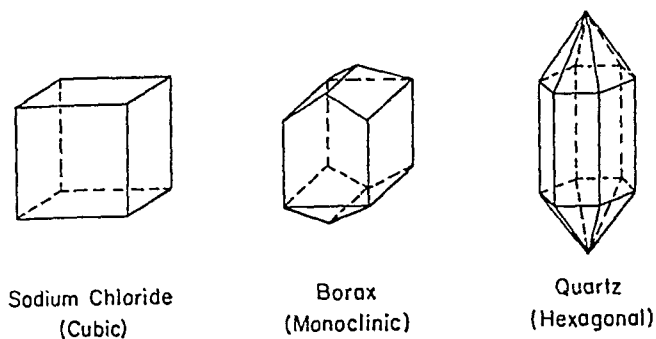


FIG. 17-6. Some Typical Crystal Habits. Reproduced with permission from Kolthoff and Elving, Treatise on Analytical Chemistry, Part I, Interscience Publishers, Inc., New York.

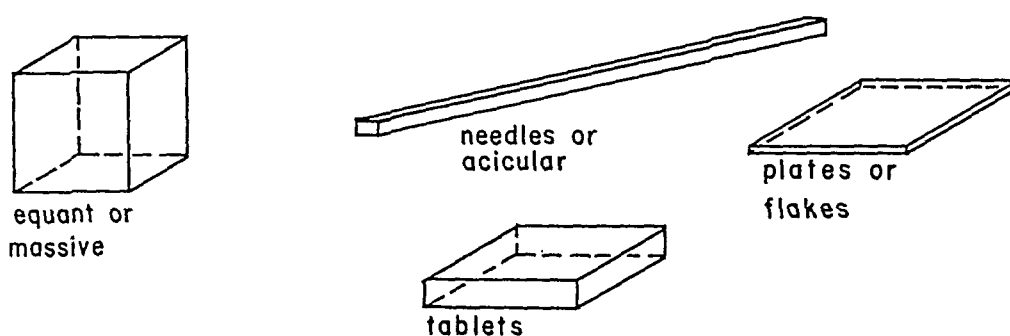


FIG. 17-7. Common Crystal Habits. Reproduced with permission from Kolthoff and Elving, Treatise on Analytical Chemistry, Part I, Interscience Publishers, Inc., New York.

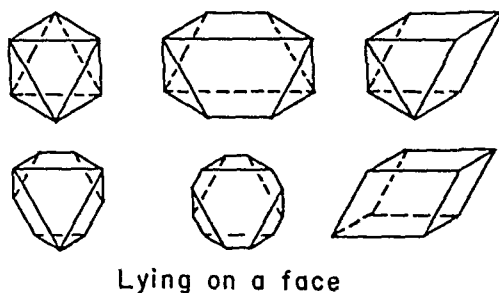


FIG. 17-8. Octahedron and Distortions. Reproduced with permission from Kolthoff and Elving, Treatise on Analytical Chemistry, Part I, Interscience Publishers, Inc., New York.

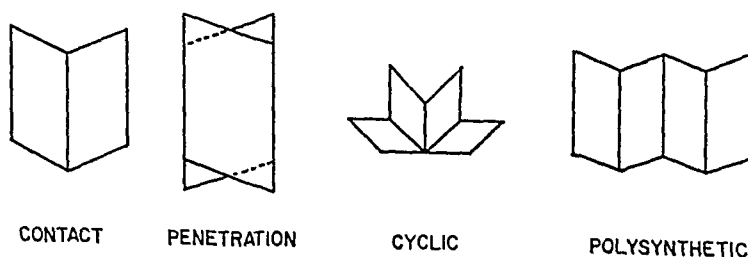


FIG. 17-9. Twinned Crystals. Reproduced with permission from Kolthoff and Elving, Treatise on Analytical Chemistry, Part I, Interscience Publishers, Inc., New York.

TABLE 17-1. REFRACTIVE INDICES OF SOME COMPOUNDS ARRANGED IN ORDER OF INCREASING MOLECULAR WEIGHT

Compound	Molecular Weight	Refractive Index
Sodium fluoride.....	42.00	1.336
Sodium chloride.....	58.45	1.5442
Sodium bromide.....	102.91	1.6412
Sodium iodide.....	149.92	1.7745

Determination of all indices on an unknown inorganic compound leads to almost certain identification, since almost all of them have been characterized with respect to refractive index, and the values have been tabulated. Too few organic compounds have been described to ensure identification, but the values nevertheless suggest molecular shape and presence or absence of highly refractive groups. For example, an organic crystal with one high and two low refractive indices is very likely a linear molecule, whereas the combination of two high indices and one low one signifies planar molecules. Three high indices indicate a highly conjugated molecule which may contain bromine, iodine, nitro, or other highly refractive groups.

Refractive index determination requires only a minute amount of sample, which can be recovered.

**Isotropy and Anisotropy.**—Only glass, some plastics, and compounds in the cubic system show a single refractive index, designated  $n$ ; they are optically *isotropic*.

Systems having two or three refractive indices, exhibiting different optical properties in different directions, show optical *anisotropy* (double refraction or birefringence). The tetragonal and hexagonal systems have two principal refractive indices: epsilon in the unique direction and omega perpendicular to it. They are therefore termed uniaxial. The systems with two isotropic directions (that is, two optic axes), the orthorhombic, monoclinic, and triclinic, have three principal refractive indices, designated alpha, beta, and gamma, in increasing order. Any refractive index between these principal values can be observed in intermediate directions.

**Refractive Index Measurement.**—The actual mechanism of refractive index measurement consists of immersing the particulate sample in a medium of known refractive index and using a narrow pencil of axial light. If the refractive indices of the medium and a particle are equal, the particle is invisible; if they differ, the particle shows relief and a bright halo, termed the Becke line, appears at the edge of the particle. On raising the focus of the microscope the Becke line shifts toward the medium of higher index. The degree of contrast shown is directly proportional to the difference in refractive index. The accuracy of the Becke test is about  $\pm 0.001$ , although  $\pm 0.0004$  is possible with monochromatic light and temperature control.

Crystal fragments with irregularly sloped edges may show two bright lines which move in opposite directions, so that the *oblique illumination* method may be preferable.\*

\* See Chamot and Mason, *Handbook of Chemical Microscopy*, Vol. I, John Wiley and Sons, Inc., New York, p. 315, 1958.

Anisotropic crystals must be studied with the help of polarized light, which has a single vibration direction perpendicular to the direction of propagation. Ordinary light can be polarized with a Nicol prism or a polarizing filter, with which most chemical microscopes are equipped. The refractive index actually observed can be controlled by rotating the crystal to the proper position relative to the vibration direction of the polarizer (Fig. 17-10).

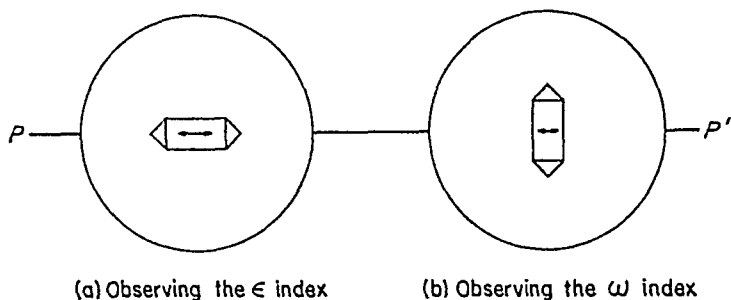


FIG. 17-10. Orientations of Tetragonal Crystal Relative to Polarizer Vibration Direction.

**Index Variation Methods.**—These methods allow the use of fewer liquid standards with a given specimen, by (1) mixing two liquids, (2) varying the wavelength of light, (3) varying the temperature, and (4) varying both wavelength and temperature.

**Mixing Two Liquids.**—Instead of mounting the particles successively in single liquids of known refractive index, they can be mounted in a liquid of somewhat higher index and small increments of a lower index liquid can be added until a match in index is observed. The index of the mixed liquid is then determined with a microrefractometer.

**Variation of the Wavelength of Light.**—Variation of the index of a substance with the wavelength of light is called *dispersion of refractive index*. Refractive indices of all solids vary with wavelength, so that this property can be used to assist in the identification of unknown solids (see Table 17-2).

TABLE 17-2

Solid	Index	Wavelength (A)		
		4861 <sup>a</sup>	5893 <sup>b</sup>	6563 <sup>a</sup>
Sodium chloride.....	$n$	1.5534	1.5443	1.5407
Quartz.....	omega	1.5497	1.5442	1.5419
Barium sulfate.....	beta	1.641	1.636	1.634

<sup>a</sup> Lines in the mercury arc.

<sup>b</sup> Sodium doublet, with average wavelength equal to 5893A.

Variation in the wavelength may be achieved by using a succession of filters, spectrally limited lamps (sodium, hydrogen, mercury, etc.) or a monochromator. Normally a sodium lamp, or at least a yellow filter, is used when measuring refractive index; hence, the indices for sodium light are of most interest. In recent years the very narrow band interference filters have come into general use. They are excellent for use in microscopy.

**Dispersion staining** is an identification technique based on the differences in dispersion of refractive index of particulate solids and the liquid media in which the solid is imbedded. Two different procedures called annular screening and central screening give colored particle boundaries. Annular screening shows a color containing those wavelengths near that at which both particle and medium show a match in refractive index; central screening shows colors complimentary to those shown by annular screening, i.e., light of wavelengths refracted by the particle in that medium.

Based on these effects it is possible to systematically identify transparent particles by their dispersion staining colors in Cargille refractive index media. Dispersion staining is a very simple technique of wide application. It greatly increases the certainty of identification and makes possible dependable analytical work by less skilled personnel. Crossmon<sup>7</sup> has applied this phenomenon intensively for analysis, and Schmidt<sup>8</sup> has used it for the analysis of dust particles. The method is most effective for those compounds which are isotropic or do not vary greatly in refractive index or dispersion with direction in the crystal. Many minerals are included in this category.<sup>9</sup>

**Variation of Temperature.**—Refractive indices of nearly all liquids and solids decrease with an increase in temperature. The index change per degree Centigrade,  $dn/dt$ , is essentially constant for each liquid over a normal range of temperatures and, once determined, can be used to calculate the refractive index of the liquid at any other temperature. On the other hand,  $dn/dt$  for most solids is negligible. In practice, the temperature of the preparation is increased until liquid and solid have the same index; the index of the liquid can then be calculated from its known temperature coefficient of refractive index,  $dn/dt$ .

**Double Variation Method.**—An even greater range of index can be obtained from a single liquid by combining the techniques of wavelength and temperature variation. This procedure is known as Emmons' double variation method.<sup>10</sup>

**Nonprincipal Refractive Indices.**—For strictly analytical purposes it is often more important to measure and publish a so-called prime or intermediate value of the refractive index rather than the principal index. This is true when the prime value is easier to obtain. Crystals of ascorbic acid usually lie on a face so that gamma prime, with a value of  $1.694 \pm 0.002$  is exhibited, whereas gamma itself,  $1.746 \pm 0.004$ , lies at an angle of  $41^\circ$  from the plane exhibited.

**Liquids for Measuring Refractive Index.**—Lists of standard immersion liquids for refractive index determinations are given in textbooks of chemical microscopy and petrography.<sup>11</sup> Directions for preparing sets of mixed liquids are given by Need-

<sup>7</sup> Anal. Chem., 20, 976, 1948.

<sup>8</sup> Staub, 41, 436-467, 1955.

<sup>9</sup> Dodge, Am. Mineralogist, 33, 541-549, 1948; Cherkasov (transl. Mitten) International Geology Review, 2, 218-235, 1960; Giabar et al., The Microscope, in press, 1962.

<sup>10</sup> Emmons, Amer. Mineral., 11, 115, 1926; 13, 504, 1928; 14, 414, 441, 482, 1929.

<sup>11</sup> Chamot and Mason, Handbook of Chemical Microscopy, Vol. 1, 1958; Hartshorne and Stuart, Crystals and the Polarizing Microscope, Arnold, London, 1960; Johannsen, Manual of Petrographic Methods, McGraw-Hill Book Co., Inc., New York, 1918.

ham.<sup>12</sup> Sets of calibrated mixed liquids can also be obtained commercially.<sup>13</sup>

**Refractive Index of Liquids.**—A detailed review of methods for measuring refractive indices of liquids is given in Weissberger.<sup>14</sup> These include simple immersion methods, the Nichols Stage Refractometer, the Jelley Microrefractometer, Abbe and Pulfrich Refractometers, and the Wright Stage Refractometer, which is described here.

The Wright stage microrefractometer consists of a pair of miniature prisms mounted on a microscope slide, so that a small gap lies between them. The angle of the prisms is  $60^\circ$  and the surface of the lower one is ground, while that of the upper one is polished. A drop of liquid is placed in the gap and a low-power objective is focused on the top of the cell. Using monochromatic light the back aperture of the objective is observed with the Bertrand lens in place. The field is divided into dark and light portions separated by a sharp dividing line—the position of this critical boundary depends on the index of the liquid and is measured with a filar eyepiece micrometer. The apparatus is calibrated with liquids of known refractive index (Fig. 17-11).

**Sign of Double Refraction.**—Anisotropic crystals resolve light into components vibrating in mutually perpendicular planes. This property is known as double refraction or birefringence.

An anisotropic crystal is described as being optically positive (+) or negative (−). For positive crystals, the epsilon refractive index is greater than the omega, or gamma minus beta is greater than beta minus alpha. For negative crystals, omega is greater than epsilon, or beta minus alpha is greater than gamma minus beta.

**Extinction.**—If a second polar, called an analyzer, is inserted into the light path above the objective and with its vibration direction perpendicular to that of the first, the field appears black, as do all isotropic materials. Anisotropic materials appear gray, white, or colored. On rotating the stage, they will disappear (become black) when their vibration directions parallel those of the two polars. The extinction positions may be parallel, symmetrical, or oblique with respect to the crystal edges (Fig. 17-12).

**Optic Axial Angle.**—By removing the eyepiece, by using a Bertrand lens, or by examining the eyepoint above the eyepiece with a magnifying glass, the image at the back aperture of the objective is observed. Each point in the field is associated with a particular direction of propagation of the illuminating light: the center represents light traveling parallel to the axis, the edge corresponds to light at a maximum angle, with intermediate angles between.

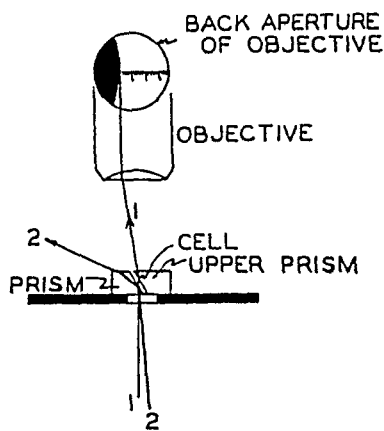


FIG. 17-11. Wright Refractometer. Reproduced with permission from Kolthoff and Elving, *Treatise on Analytical Chemistry*, Part I, Interscience Publishers, Inc., New York.

<sup>12</sup> Needham, *The Practical Use of the Microscope*, Charles C Thomas, Publisher, Springfield, Ill., 1959.

<sup>13</sup> Available from R. P. Cargille Laboratories, New York. Indices from 1.35 to 2.11, with temperature coefficient and dispersion noted on each bottle.

<sup>14</sup> *Physical Methods of Organic Chemistry*, Vol. I, Interscience Publishers, Inc., New York, 1945.

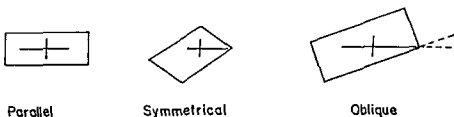


FIG. 17-12. Extinction in Anisotropic Crystals. Reproduced with permission from Kolthoff and Elving, *Treatise on Analytical Chemistry*, Part I, Interscience Publishers, Inc., New York.

An anisotropic crystal observed by this method displays between crossed polars a pattern of polarization colors corresponding to the full cone of directions by which the crystal is illuminated. Superimposed on this pattern will be the pattern of extinction positions. The combination of the two is the *interference figure*.

For biaxial crystals, the acute angle between the two axes, designated  $2V$ , can be estimated or calculated from the distance between the black brushes<sup>15</sup> (Fig. 17-13).

Variation of the size of the optic axial angle in a given interference figure is known as *dispersion of the optic axes*. It is usually visible in white light as a tinge of color at either edge of the dark brushes—the optic axial angle for the color of light on the convex side is greater than that for the color of light on the concave side.

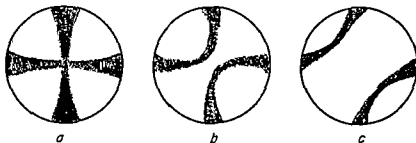


FIG. 17-13. Centered Uniaxial (a) and Biaxial Interference Figures with Small  $2V$  (b) and Large  $2V$  (c). Reproduced with permission from Kolthoff and Elving, *Treatise on Analytical Chemistry*, Part I, Interscience Publishers, Inc., New York.

**Pleochroism.**—Some colored anisotropic substances selectively absorb light differently for different vibration directions, and are termed pleochroic. In polarized light but not crossed polars, they change color as the stage is rotated.

### C. CHEMICAL REACTIONS

Where microchemical testing is required, a general or specific reagent can be added to a test drop containing the unknown. The reaction product can then be recognized by morphology and/or simple optical properties.

Chamot and Mason<sup>16</sup> have compiled a large number of precipitation reactions for the microscopic analysis of inorganic anions and cations. The tests are especially applicable to the analysis of complex mixtures. Descriptions and photomicrographs of the reaction products are included, as well as detailed manipulative

<sup>15</sup> Chamot and Mason, *Handbook of Chemical Microscopy*, Vol. I, p. 304, 1958.

<sup>16</sup> *Handbook of Chemical Microscopy*, Vol. II, John Wiley and Sons, Inc., New York, 1939.

methods. A few examples of the reagents used to test for specific ions are listed in Table 17-3.

TABLE 17-3. PRECIPITATION REAGENTS USED BY CHAMOT AND MASON TO DETECT INORGANIC IONS

<i>Ion</i>	<i>Reagents</i>
Sodium.....	Uranyl acetate, zinc uranyl acetate
Potassium.....	Chloroplatinic acid, perchloric acid
Ammonium.....	Chloroplatinic acid, iodic acid
Beryllium.....	Chloroplatinic acid, potassium oxalate
Calcium.....	Ammonium carbonate, sulfuric acid
Strontium.....	Ammonium carbonate, iodic acid
Barium.....	Ammonium carbonate, potassium ferrocyanide
Magnesium.....	Ammonium hydroxide and phosphate
Zinc.....	Oxalic acid, potassium mercuric thiocyanate
Copper, lead.....	Zinc, potassium, mercuric thiocyanate
Mercury.....	Potassium bichromate, lead
Aluminum.....	Ammonium bifluoride, cesium sulfate
Tin.....	Zinc, cesium chloride
Arsenic.....	Ammonium molybdate, cesium sulfate and potassium iodide
Chromium.....	Silver nitrate, lead acetate
Uranium.....	Thallous nitrate and ammonium carbonate
Iron.....	Potassium ferrocyanide, potassium thiocyanate
Fluoride.....	Sodium fluosilicate
Carbonate.....	Silver nitrate, calcium acetate
Nitrate.....	Nitron sulfate (diphenylendianilodihydrotriazol)
Cyanide.....	Silver nitrate, ammonium sulfide and ferric chloride
Chloride.....	Silver nitrate, thallous nitrate

Corresponding procedures have been applied to some organic systems using reagents to form addition compounds. The sample and reagent are melted on a microscope slide, adjacent to and touching each other. By this procedure picric acid forms deeply colored molecular addition compounds with most of the polynuclear aromatic hydrocarbons; hence very small samples containing a few per cent of either the hydrocarbon or picric acid can be characterized as such by melting in contact with the other. 2,4,7-Trinitrofluorenone<sup>17</sup> can also be used as a test reagent for many aromatic derivatives.

Crozier and Seely<sup>18</sup> have developed a method for testing suspended dust samples for particular contaminants. The suspended dust is impinged onto a microscope slide coated with a gelatin film containing a specific reagent in solution. To test for sodium chloride, the gelatin is impregnated with mercurous fluosilicate. After a short time, a number of white halos of mercurous chloride appear in the gelatin, each halo surrounding the original location of a single chloride particle. The thickness of the halo is a measure of the size of the original particle. Extremely

<sup>17</sup> Laskowski and W. C. McCrone, *Anal. Chem.*, **26**, 1497, 1954.

<sup>18</sup> *Anal. Chem.*, **24**, 577, 1952.

in 1891 described many of these techniques including the "contact method" (*mixed fusion*) for the determination of identity or lack of identity of two compounds.

The mixed fusion, a very useful technique, requires fusion of the components on opposite sides of the cover slip so that they mix in the center. The resulting zone of mixing shows, as a result, a complete and continuous composition gradient.

The *identification* of fusible compounds by fusion methods is very rapid, consumes only small quantities of material, and requires relatively little specialized training or equipment. An unknown compound in a limited category (e.g., polynitro compounds) can usually be identified in less than 5 minutes, if that compound has once been studied by fusion methods. There are so many characteristic properties that can be observed on crystals from the melt that one or two easily recognized and typical properties (anomalous polarization colors, unique shrinkage cracks or gas bubbles, crystal habit, transformation mechanism) can be remembered for each compound, hence a complete check of all properties is not usually necessary.

In the United States this means of identification has been applied to relatively small groups of compounds: substituted aminoquinolines,<sup>21</sup> sterols,<sup>22</sup> high explosives,<sup>23,24</sup> hexachlorobenzenes,<sup>25</sup> polynuclear aromatics,<sup>26</sup> synthetic polymers,<sup>27</sup> alcohols,<sup>28</sup> and paper chemicals.<sup>29</sup>

The characteristics observed cannot be recorded in tabular fashion and only with difficulty in descriptive terms.

The Koflers have approached the problems of tabulation as shown in Table 17-4.

In the complete tables, which include about 1200 compounds, the primary tabulating characteristic is the *melting point*, or the best possible substitute, for those compounds which decompose or sublime before melting. Then, since most decomposable compounds are stable somewhat below the melting point, the Koflers have introduced the *eutectic melting temperature* with two standard compounds, giving three numerical constants characteristic of each compound.

**Determining the Melting Point.**—Providing the test compound does not sublime or decompose first, continued heating causes the sample to melt, changing quickly to a liquid. The temperature at which the last crystals melt is taken as the melting point (Fig. 17-15).

The sample particles should be small and well separated, covering about 10% of the field with crystals smaller than 325 mesh (44 microns). A fraction of a milligram of sample on a half-slide can be simultaneously crushed and dispersed by pressing a cover slip against it with a rotary movement, using a pencil eraser. The cover glass must then be cleaned and replaced, as crystals adhering to the underside of it consistently melt 1°C. higher than those on the slide.

To determine the *equilibrium melting point*, the hot stage (or cold stage) is heated and cooled very slowly over a narrow temperature range. The preparation,

<sup>21</sup> Goetz-Luthy, J. Chem. Education, 26, 159, 1949.

<sup>22</sup> Gilpin, Anal. Chem., 23, 365, 1951.

<sup>23</sup> McCrone, W. C., Andreen, and Tsang, Microscopic Examination of High Explosives and Boosters, OSRD Report No. 3014, August 1, 1944.

<sup>24</sup> McCrone, W. C., Microchemical Journal, III, 479, 1959.

<sup>25</sup> Arceneaux, Anal. Chem., 23, 906, 1951.

<sup>26</sup> Laskowski, Grabar, and McCrone, W. C., Anal. Chem., 25, 1400, 1953; Laskowski and McCrone, W. C., *ibid.*, 26, 1497, 1954, and 30, 542, 1958.

<sup>27</sup> Grabar and Haessly, Anal. Chem., 28, 1586, 1956.

<sup>28</sup> Laskowski and Adams, Anal. Chem., 31, 148, 1959.

<sup>29</sup> Gilpin, TAPPI, 43, 423, 1960.



TABLE 17-4. EXCERPT FROM KOFLER'S TABLES FOR THE IDENTIFICATION OF ORGANIC COMPOUNDS

Melting Point, °C.	Substance	Eutectic Temp. with		Glass Powder	Temp., °C.	Miscellaneous Characteristics
		Azo-benzene	Benzil			
95	Carbon tetrabromide	54	40	1.5898	111-113	Sublimes strongly above 30°C. to give plates and rosettes having scalloped edges, above 46°C. gives isotropic honeycomb.
95	3-Methyl indole (Skatole)	43	44	1.5700 1.5611	100 121	Odor, sublimes above 50°C. Gives thin rounded plates.
95	4,6-Dichlororesorcinol	50	46	1.5700	95-97	Usually colored brown, above 55°C. sublimes giving needles; long needles from the melt.
96	Methyl <i>p</i> -nitrobenzoate	51	63	1.5101 1.5000	111-112 130	Yellow, sublimes above 70°C. to give rhombs.

a small sized droplet (preferably about 1 mm. or less in diameter), under the cover glass, is allowed to crystallize and then placed in a hot stage already heated to a point just below the melting point. The stage is then heated at a rate of about 1°C. per minute until the crystals are partly melted, then allowed to cool until crystallization just begins. Heating is recommenced at the instant, or just before, the crystals begin to grow, and is stopped as, or just before, they begin to melt. The equilibrium melting point is given as the midpoint of the range between which growth and melting occur. These two temperatures usually lie about 0.2° to 0.3°C. apart. One word of caution, however: the melting point so accurately determined by this means is characteristic of the percentage of the sample actually melted and may vary many degrees depending on the extent of melting if the compound is impure.

**Eutectic Melting Temperature.**—The eutectic melting temperature is ordinarily observed on a mixed fusion preparation (Fig. 17-16) with the second components chosen from the following list, depending on the melting point of the test compound.

<i>For Melting Points in °C. Between</i>	<i>Standard Second Component</i>
20-100.....	Azobenzene, benzil
100-120.....	Benzil, acetanilide
120-140.....	Acetanilide, phenacetin
140-170.....	Phenacetin, benzanilide
170-190.....	Benzanilide, salophen
190-240.....	Salophen, dicyandiamide
240-340.....	Phenolphthalein

The eutectic in the zone of mixing will, of course, always melt at a temperature lower than that of either component.



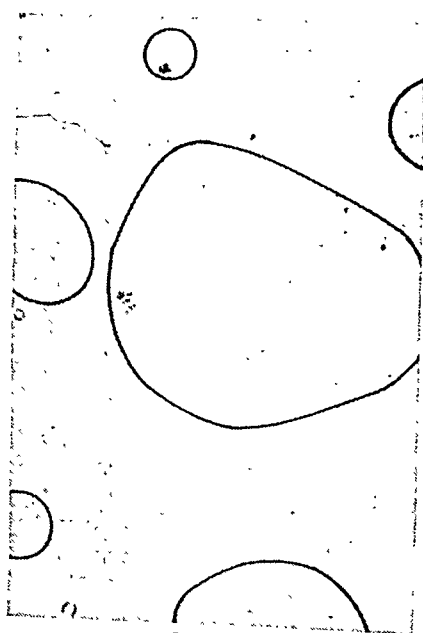
68°C.



68.2°C.



68.4°C.



68.5°C.

FIG. 17-15. Photomicrographs Taken During Melting of Very Pure Azobenzene. Reproduced with permission from *Fusion Methods in Chemical Microscopy*, Interscience Publishers, Inc., New York, 1957.

**Refractive Index of the Melt.**—In order to make identification even more certain, the Koflers have developed a technique for measuring the *refractive index of the melt* by using glass powder standards covering the range 1.43 to 1.69 in increments of about 0.01. The refractive index is determined by observing the temperature at which the glass powder standard has the same index as the melt. This temperature is, of course, quite unique, although the compound must be very pure. Occasionally, when the compound decomposes, it is possible to bracket the refractive index between two of the glass powder standards. For example, the melt of phenylthiourea has a refractive index at the melting point between 1.6231 and 1.6353.

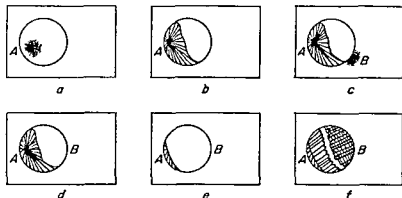


FIG. 17-16. Operations Involved in a Mixed Fusion: (a, b) the high melting component, *A*, is fused under a cover glass and allowed to resolidify; (c) the low-melting component, *B*, is placed at the edge of the cover glass and (d) heated so that it melts and runs under the cover glass; (e) the prep is reheated until all of *B* and most of *A* are melted; (f) as the prep cools, the crystal fronts of *A* and *B* grow towards the zone of mixing. Reproduced with permission from *Fusion Methods of Chemical Microscopy*, Interscience Publishers, Inc., New York, 1957.

Miscellaneous identifying characteristics are also listed, e.g., sublimation temperature, polymorphic transformations, form, and habit of the sublimed crystals of crystals from the melt, color, odor, etc.<sup>30</sup>

**Mixed Fusion.**—A mixed fusion gives a rapid and dependable means of determining whether two given samples are the same compound. The known and unknown are made the two components in a mixed fusion, and the crystal front of the higher melting component is observed as it grows toward the zone of mixing. If the two are identical, the crystal front will continue to grow through the zone of mixing with no discontinuity in rate of growth or form of the crystals. A difference in purity may cause a change in the rate of growth and, perhaps, crystal size, as the crystal front progresses through the zone of mixing. If the two components are different there will always be a discontinuity in the rate of crystal growth, and the type of crystals will usually change radically in the zone of mixing.

### III. TECHNIQUES OF PREPARATION AND PURIFICATION

**Surfacing and Sectioning.**—Soft materials can usually be surfaced (for examination in reflected light) or sectioned (for transmitted light) by cutting with a sharp

<sup>30</sup> The data have been retabulated into a more useful analytical form, included in McCrone, W. C., *Fusion Methods in Chemical Microscopy*, Interscience Publishers, Inc., New York, 1957.

knife or razor. The specimen should not be deformed or compressed during cutting; a microtome allows more accurate control of the operation. Friable materials may be first embedded in paraffin or collodion.

Hard materials such as metals, minerals, and ceramics can be surfaced or sectioned by abrasion with progressively finer abrasive materials.

These methods are used by petrologists in the study of rocks and minerals, and are described in detail in textbooks of practical petrology.

**Staining Methods.**—The visibility of specimens can be increased by the application of stains. Most of these are organic dyestuffs, which are selectively absorbed by the different materials in the sample, or which act like chemical reagents, revealing chemical differences between portions of the specimen.

The most common is Herzberg's stain, an aqueous solution of zinc chloride, potassium iodide, and iodine, which selectively colors fibers having different origins or treatments, and Gram's stain (of which there are modifications) for differentiating between types of bacteria, in which alcoholic crystal violet (or gentian violet) stain is fixed to bacteria with iodine solution. Some bacteria can be subsequently decolorized with alcohol.

The etching reagents used on metallic specimens also allow a differentiation of constituents and interpretation of structure. The etchant may be a selective solvent, it may oxidize certain constituents, may deposit colored material, attack the boundaries of crystal grains, or develop microscopic etch pits on them.

**Mounting in a Medium of Proper Refractive Index.**—Substances with different refractive indices can be differentiated by choosing a mounting medium of the same or nearly the same refractive index as one of the components, and markedly different from the other, so that the first will be invisible while the other shows strong relief.

For example, refractive index and/or birefringence are useful in determinations of HMX in preparations of the high explosive RDX. The sample is mounted in a liquid having a refractive index of about 1.590 (Fig. 17-17). Since all three refractive indices of RDX are close to 1.590, it shows very low contrast in ordinary white light, while HMX, with one index near 1.590 and two much higher indices, shows strong contrast (enhanced in certain positions with one polar).

**Mechanical Separation.**—The most direct and best method of separation would be to pick out the desired component with a clean needle, under the microscope. Other physical means such as magnetic separation or flotation could also be employed, as described by Chamot and Mason.<sup>31</sup>

**Solvent Extraction.**—Finely divided particles may require solvent extraction for separation. The apparatus illustrated has been found very satisfactory (Fig. 17-18). The drawn-out tip of a medicine dropper containing the sample is supported in a closed vial containing a drop of solvent (to saturate the space with solvent vapor). The solvent is added dropwise, at intervals of several minutes. Extraction is complete when a freshly extracted micro drop is allowed to evaporate on a clean microscope slide, and leaves no residue.

The following solvents, in the order listed, have been found most useful: water, ether or benzene, 5% sodium hydroxide, 5% hydrochloric acid, dimethylformamide, and nitromethane.

The sample is recovered by slowly evaporating the extracted solution to dryness.

<sup>31</sup> Handbook of Chemical Microscopy, Vol. I, p. 141, 1958.

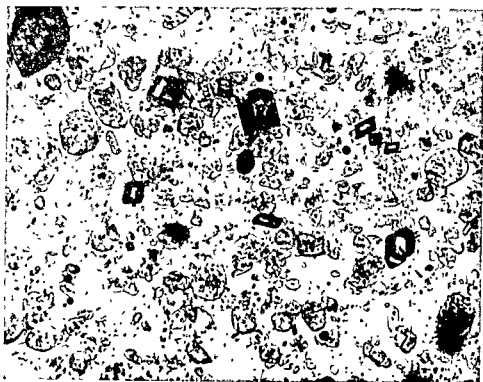


FIG. 17-17. Crystals of RDX (Low Contrast) and HMX (High Contrast) Mounted in a Liquid of Refractive Index 1.590. Reproduced with permission from *Fusion Methods of Chemical Microscopy*, Interscience Publishers, Inc., New York, 1957.

**Chromatography.**—Chromatographic separations of micro quantities can be carried out in a column such as the one described for solvent extraction. Standard adsorbents such as silica gel, alumina, charcoal, etc., can be used with any of the common solvents, although those of intermediate polarity, such as acetone, ethanol, or water, usually function best. The lower end of the column is plugged with glass wool. The adsorbent, in paste form with the solvent to be used, is drawn into the column by suction and the solution to be chromatographed is poured in at the top. The issuing solution can be allowed to drop onto a slide beneath it, the slide being on a hot bar at a temperature slightly below the solvent's boiling point. A metal block with an opening in the center placed under the slide prevents the solution from spreading.

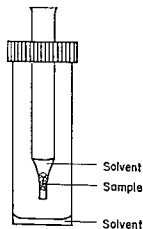


FIG. 17-18. Simple Apparatus for Solvent Extraction.

Paper chromatography is recommended for samples in the range of  $10^{-6}$  to  $10^{-12}$  g. The sample is placed on a small strip of filter paper ( $\frac{1}{4} \times 1\frac{1}{4}$  in.), previously washed chromatographically with carefully purified solvent. The paper is wetted with solvent, placed between two glass slides, and suspended over a surface of pure solvent (Fig. 17-19). The solvent passes up along the paper and evaporates from the upper tip. For solvents boiling in the range of  $60^\circ$  to  $100^\circ\text{C.}$ , about 30 minutes will be required; proportionately longer times are required for higher boiling solvents.

The paper is allowed to dry completely by removing one of the glass slides. When dry and separated, the slides should be carefully examined, because a minute dried deposit of crystals may betray the position of at least one of the separated components. A narrow strip lengthwise of the paper can be cut off and tested with a reagent. A strip about 1 mm. wide from the middle of the paper is best, since most of the sample is contained along the vertical edges of the paper strip.

Finally the paper strip is separated along the obvious demarcation lines or along  $\frac{1}{4}$  in. lengths and extracted individually with solvent.

**Distillation.**—Distillation can be carried out on several microliters of liquid in the bottom of a glass tube of 20 to 30 mm. length and 2 to 3 mm.

inside diameter. On heating, a ring of distillate creeps up the tube wall; heating is stopped when it reaches nearly to the top. The tube is then laid horizontally on a cold surface so that the distillate collects in a small droplet, which is picked up with a glass capillary. Comparison of the refractive indices (by the glass powder method) of the original sample and the first distillate fraction will indicate whether or not the original sample is pure or a mixture.

**Filtration.**—Filtration of microscopic particles can be carried out with slide and cover slip. The sample is placed at the edge of the cover slip and the liquid flows under leaving the particles at the edge. The particles may be washed with successive micro drops of solvent. The "filtrate" may be removed by touching with a filter paper. In the same way a fusible component can be separated from a mixture by heating it at the edge of a cover slip until one component melts and flows under the cover slip.

A very fine capillary, 10 to 20 microns inside diameter, can be used to filter very small drops if the suspended particles are not too fine. Small samples can also be filtered by placing the drop (or melting the fusible portion of the sample) on a small square of hardened filter paper. The residue can then be removed mechanically and the filtrate can be extracted from the paper with a solvent.

**Crystallization from Solution by Evaporation.**—The compound, usually inorganic, to be crystallized is stirred into a drop of solvent, usually water, on a slide. Warming the slide will of course hasten solution but must not be overdone to the point of hastening evaporation. Enough of the compound is added to saturate the solution. Upon evaporation at room temperature, crystals begin to form at the edges of the drop. These tend to be malformed and should be pushed to the center with the fine tip of a glass rod. When it is completely saturated, well-formed crystals will begin to grow throughout the drop (Fig. 17-20).

The crystals can be manually separated from the solution by pushing them out of the drop with a fine glass rod, or by draining off the liquid with a piece of hardened filter paper.

**Crystallization from Solution by Cooling.**—Organic compounds may be recrystallized from a drop on a microscope slide if high boiling and high surface tension solvents are used. The drop must be saturated at room temperature but with sufficient excess solute so that the drop may be heated to about 35°C. to dissolve

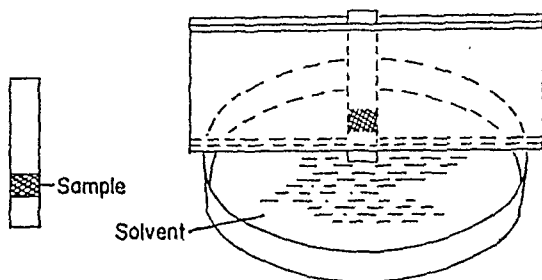


FIG. 17-19. Paper Chromatography Between Two Microscope Slides.

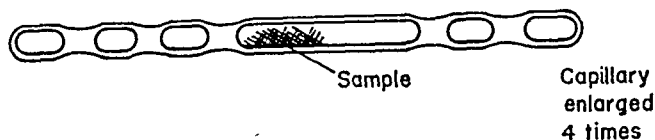


FIG. 17-22. Appearance of Capillary After Several Sublimations.

**Thermal Diffusion.**—A slide containing a layer of melt 1 mm. x 5 mm. x 25 microns with a cover glass about 1 x 5 mm. is placed over the light well of the hot stage. An equilibrium melting point is taken with 50% of the sample melted. Any change in melting point indicates the presence of a mixture: an increase shows the impurity is migrating toward the hotter end of the sample; a decrease denotes migration to the cooler region, directly over the light well. When the melting point ceases to change, the preparation is cooled and allowed to crystallize, preventing remixing. The desired component is removed mechanically with a needle, and the process can be repeated. When the equilibrium melting range from 10 to 90% melted is less than 0.5°C., the sample is reasonably pure.

**Absorption Purification.**—L. Kofler<sup>33</sup> has devised a purification technique based on the fact that, on heating, any mixture will melt partly to a liquid containing all the impurities, and one solid component in excess. This solid component can be isolated if the eutectic melts are soaked into a porous medium, such as filter paper.

In practice, not more than 100 mg. of sample are placed on a square centimeter of hardened filter paper on a half-slide, and covered with a second half-slide arranged crosswise to the first. The "sandwich" is placed on a hot bar and slowly moved toward higher temperatures until the sample just begins to melt, as indicated by a wet spot on the filter paper surrounding the solid sample. Movement of the slide is stopped, the upper half-slide is pressed to squeeze the eutectic melt into the filter paper, and the upper half-slide with the adhering solid sample is removed. Repeating the procedure a few times at successively slightly higher temperatures leaves solid crystals pure enough for melting-point determinations, refractive index of the melt, etc.

Filter paper may be used for mixtures heated as high as 300°C. if not held too long at that temperature. Clay plates have been used at temperatures in this range and higher.

The technique can be modified by melting the sample in a carefully heated hot stage, using a cover slip for the upper half-slide.

A second modification of this technique requires that the sample be mounted on the end of a very fine capillary (less than 20 microns inside diameter). On heating, the eutectic melt will be drawn into the capillary first, leaving the partly purified crystals of the highest melting component atop the capillary. By carrying out the procedure over a period of a few minutes, the entire sample can be drawn into the capillary, the last portion to enter being quite pure. The capillary should be cooled quickly and allowed to crystallize to avoid further diffusion. The end containing the pure compound can then be broken off and the compounds removed and studied.

**Adsorption-Sublimation.**—One of the most useful devices for purification of mixtures has been suggested by W. Kofler,<sup>34</sup> based on gas-phase chromatography.

<sup>33</sup> Kofler, L., and Wannenmacher, Ber. Deut. Chem. Ges., 73, 1388, 1940.

<sup>34</sup> Monatsh. Chem., 80, 694, 1949.

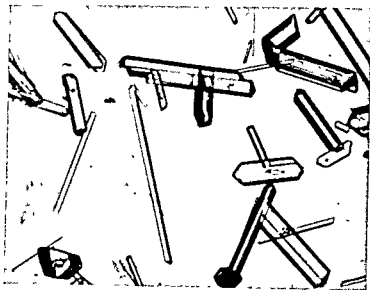


FIG. 17-20 Crystallization on a Microscope Slide. Reproduced with permission from *Fusion Methods of Chemical Microscopy*, Interscience Publishers, Inc., New York, 1957.

additional solute. On slow spontaneous cooling well-formed crystals should slowly grow although seeding by scratching with the glass tip may be necessary.

**Crystallization by Sublimation.**—Volatile organic compounds can be recrystallized (or separated from a mixture) by sublimation, if care is taken to avoid decomposition. Unstable polymorphs may be obtained in this manner, especially when a cold condensing surface is used.

A slide containing the compound is heated with a microburner or hot plate, and the sublimate is allowed to collect on another slide or on a cover slip directly above. Heating is stopped when a sublimate appears, and it can then be studied for characteristic crystal angles and other morphological features.

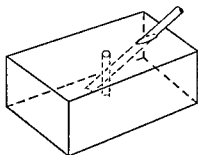


FIG. 17-21. Heating Block for Sublimation in a Capillary.

( $\frac{1}{16}$  in. diameter) through the heating operation (Fig. 17-21).

It is often a good idea to resublime a given component several times starting with an evacuated capillary about 30 mm. long and sealing off the residue each time. The capillary may be inverted between sublimations until the final capillary has the appearance shown in Fig. 17-22.

For extremely volatile substances, the receiving slide may have to be cooled by dropping cold water on it with a micropipet, or by using a chilled block. To avoid loss of material, sublimation can be carried out in a closed system. Even in a sealed glass capillary, substances with low vapor pressure can be sublimed under reduced pressure.<sup>32</sup>

For very small samples, sublimation can be carried out in a capillary tube by sealing the sample in one end, preferably under vacuum, and heating the capillary in a metal block so that the sample becomes heated while the upper portion of the capillary remains cool. A small vertical opening block permits observation of the sample during the

<sup>32</sup> Hartshorne and Stuart, *Crystals and the Polarizing Microscope*, p. 238, 1960.



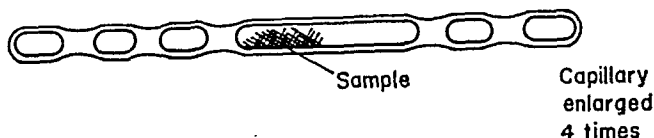


FIG. 17-22. Appearance of Capillary After Several Sublimations.

**Thermal Diffusion.**—A slide containing a layer of melt 1 mm. x 5 mm. x 25 microns with a cover glass about 1 x 5 mm. is placed over the light well of the hot stage. An equilibrium melting point is taken with 50% of the sample melted. Any change in melting point indicates the presence of a mixture: an increase shows the impurity is migrating toward the hotter end of the sample; a decrease denotes migration to the cooler region, directly over the light well. When the melting point ceases to change, the preparation is cooled and allowed to crystallize, preventing remixing. The desired component is removed mechanically with a needle, and the process can be repeated. When the equilibrium melting range from 10 to 90% melted is less than 0.5°C., the sample is reasonably pure.

**Absorption Purification.**—L. Kofler<sup>33</sup> has devised a purification technique based on the fact that, on heating, any mixture will melt partly to a liquid containing all the impurities, and one solid component in excess. This solid component can be isolated if the eutectic melts are soaked into a porous medium, such as filter paper.

In practice, not more than 100 mg. of sample are placed on a square centimeter of hardened filter paper on a half-slide, and covered with a second half-slide arranged crosswise to the first. The "sandwich" is placed on a hot bar and slowly moved toward higher temperatures until the sample just begins to melt, as indicated by a wet spot on the filter paper surrounding the solid sample. Movement of the slide is stopped, the upper half-slide is pressed to squeeze the eutectic melt into the filter paper, and the upper half-slide with the adhering solid sample is removed. Repeating the procedure a few times at successively slightly higher temperatures leaves solid crystals pure enough for melting-point determinations, refractive index of the melt, etc.

Filter paper may be used for mixtures heated as high as 300°C. if not held too long at that temperature. Clay plates have been used at temperatures in this range and higher.

The technique can be modified by melting the sample in a carefully heated hot stage, using a cover slip for the upper half-slide.

A second modification of this technique requires that the sample be mounted on the end of a very fine capillary (less than 20 microns inside diameter). On heating, the eutectic melt will be drawn into the capillary first, leaving the partly purified crystals of the highest melting component atop the capillary. By carrying out the procedure over a period of a few minutes, the entire sample can be drawn into the capillary, the last portion to enter being quite pure. The capillary should be cooled quickly and allowed to crystallize to avoid further diffusion. The end containing the pure compound can then be broken off and the compounds removed and studied.

**Adsorption-Sublimation.**—One of the most useful devices for purification of mixtures has been suggested by W. Kofler,<sup>34</sup> based on gas-phase chromatography.

<sup>33</sup> Kofler, L., and Wannemacher, Ber. Deut. Chem. Ges., 73, 1388, 1940.

<sup>34</sup> Monatsh. Chem., 80, 694, 1949.

measurement. With the scale superimposed on the specimen image, measurements can be made by direct observation, photography, or projection.

Where the particles are not of a uniform size, the count is tallied with respect to a size range, 6 to 12 size classes being represented. The details of this analysis and the calculations can be found in Volume I of Chamot and Mason.

A counting analysis can be applied to mixtures of substances with varying particle sizes by measuring the average diameter of each before counting. The results are then expressed as weight percentages according to the formula:

$$\text{Weight \%} = \frac{D_A \cdot \Sigma n_A d_A^3}{D_A \cdot \Sigma n_A d_A^3 + D_B \cdot \Sigma n_B d_B^3 + \dots} \times 100$$

where  $D$  = density of the components,  $A$  or  $B$

$d$  = average diameter of the particles with respect to weight

$n$  = number of particles

This method is often applied to the analysis of fiber mixtures and is then termed a "dot count" because the tally of fibers is kept as the preparation is moved past a point or "dot" in the eyepiece.

Counting all of one constituent in a measured amount of sample is feasible in specialized situations, such as bacterial counts. Counting cells facilitate measuring the correct sample size and are often ruled to allow systematic viewing of the entire sample.

**Reference Substances.**—A definite amount of a *reference substance*, containing a known number of particles per gram, can be added to a given weight of powdered sample, and mixed in suspension for counting. Particles of both are then counted, the count of the reference particles being a measure of the actual weight of sample being counted. Lycopodium can be used as reference for potato and rice starch mixtures, and blood corpuscles for bacteria in milk.

Young and Roberts<sup>35</sup> suggest the automatic counting and sizing of particles at the rate of a million per second, using flying spot microscopy. In this process the minified image of a scanning beam, transmitted in a reverse direction through the microscope condenser, converts any attenuation or interruption of the light energy into a proportional amount of electrical energy, which is in turn fed to counting circuits for data presentation.

The relative amounts of particulates can also be accurately measured by casting the mixture in plastic, cutting or polishing to give a plane section, and applying the method of areal analysis described below.

**Areal Analysis.**—Any sample viewed as a section, and in which the components can be differentiated, may be quantitatively analyzed by areal analysis. Used principally in metallography, where polished sections of alloys show relative areas of different phases proportional to their volume ratios, this method is also useful, in special cases, for fusion preparations. It is limited, however, to samples containing components wholly insoluble in each other, e.g., high explosives systems such as Amatol (TNT and ammonium nitrate), or RDX and wax (Fig. 17-25).

The analysis itself can be carried out in a variety of ways which will give the relative areas of the components. A drawing camera often is used to draw several representative fields onto crosshatched paper, after which the number of squares representing each component is counted. Photomicrographs of several fields can be taken; the components are then cut apart with scissors or a razor blade, sorted,

<sup>35</sup> Nature, 167, 231, 1951.

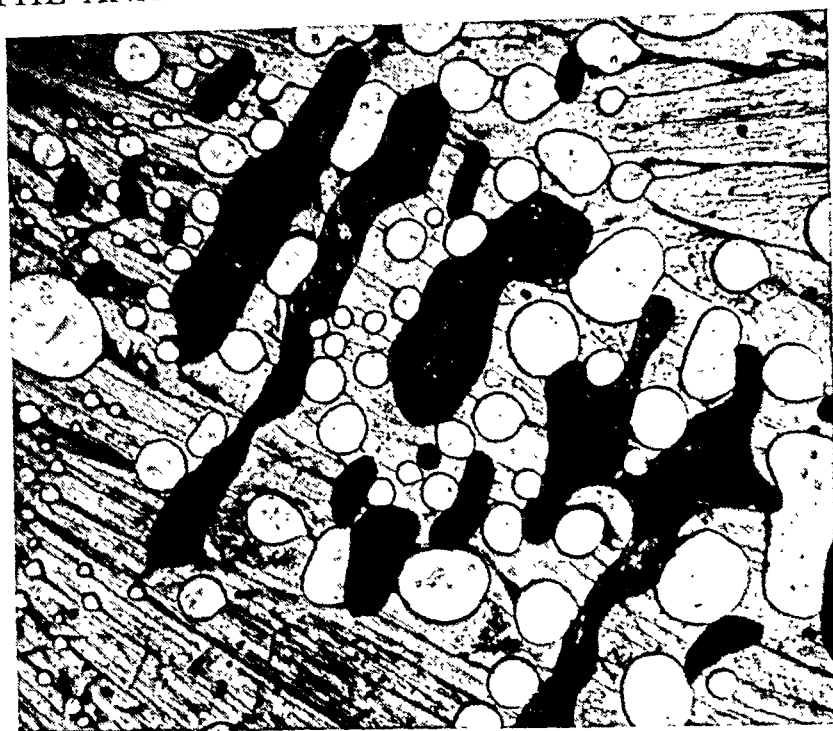


FIG. 17-25. Thin Crystalline Film of Amatol Suitable for Areal Analysis. Reproduced with permission from *Fusion Methods of Chemical Microscopy*, Interscience Publishers, Inc., New York, 1957.

and weighed separately. The percentage composition by weight can be calculated from volume percentage using the known densities.

**Physical Properties in Isomorphous Solid Solutions.**—When two compounds form a continuous series of isomorphous solid solutions the crystal properties (optical, morphological, and X-ray) vary continuously from the properties of one to the properties of the other, depending only on composition. The variation in optic axial angle of a mixed crystal has been applied to the quantitative analysis of the *p*-bromoanilides of acetic and propionic acids, and the 2,4-dinitrophenylhydrazones of acetaldehyde and propionaldehyde.<sup>36,37</sup>

**Crystal Habit Change.**—The crystal habit of a compound grown from the melt is reproducibly affected by impurities. This can serve as the basis for analysis in a binary system such as adipic acid containing up to 2% succinic acid.<sup>38</sup> Habit variations attributable to temperature are eliminated by careful control (Fig. 17-26).

**Crystallization Velocity Change.**—The rate of crystallization is dependent on the composition, the temperature, and the experimental conditions (capillary, glass tube, microscope slide). Keeping the latter two constant permits the determination of the composition by measuring the crystallization velocity, as has been successfully accomplished for *p,p'*-DDT in technical DDT.<sup>39</sup> The principal component, *p,p'*-DDT, is usually present to the extent of 70 to 80%, the remainder consisting of a complex mixture of isomers and by-products.

**Freezing-Point Depression.**—In a binary system the depression of freezing point can be used as a precise measure of composition. Bryant<sup>37</sup> has used this method

<sup>36</sup> Bryant, J. Am. Chem. Soc., 60, 1394, 1938.

<sup>37</sup> Ibid., 55, 3201, 1933.

<sup>38</sup> Mitchell, Anal. Chem., 21, 448, 1949.

<sup>39</sup> McCrone, W. C., Smedal, and Gilpin: Anal. Chem., 18, 578, 1946.



100%



99.75%



99.50%



99.25%

FIG. 17-26. Photomicrographs of Adipic Acid-Succinic Acid Mixtures Showing the Effect of Small Percentages of the Latter on the Crystal Habit of Adipic Acid. Reproduced with permission from *Fusion Methods of Chemical Microscopy*, Interscience Publishers, Inc., Inc., New York, 1957.

in a system showing solid solutions: *p*-bromoanilides of acetic and propionic acid (Fig. 17-27). Many analysts have used the same procedure for systems showing eutectic formation. Unfortunately, each system must be calibrated precisely since the molar depression of freezing points varies, at the worst, about tenfold. A depression of 0.5°C. for every weight per cent is usually used for very rough approximations of composition.

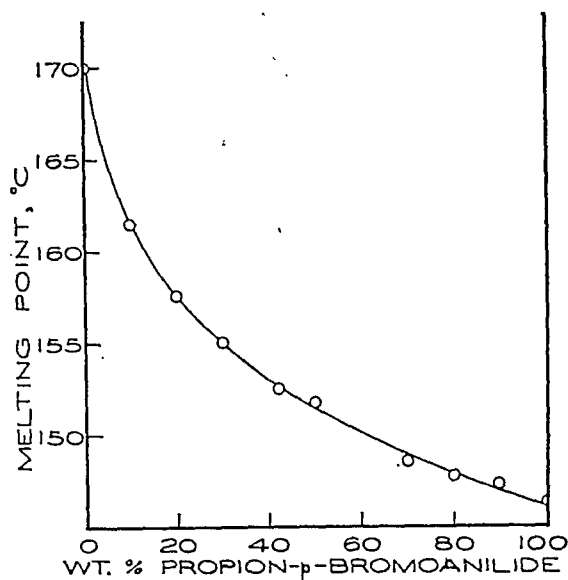


FIG. 17-27. Melting Point as a Function of Composition in a System Showing Solid Solution; Acet- and Propion-*p*-Bromanilides. (Courtesy of W. M. D. Bryant.) Reproduced with permission from Fusion Methods of Chemical Microscopy, Interscience Publishers, Inc., New York, 1957.

**Refractive Index of the Melt.**—Binary mixtures can be analyzed by measuring the refractive index of the melt.<sup>40</sup>

A standard curve is prepared for each system, in which the temperature, at which the refractive index of the melt and a glass standard are identical, is plotted against composition for the pair of compounds. Where one glass powder covers the desired range, it is necessary only to draw a straight line between the temperature for the two pure components, plus at least one other value to be certain the relationship is linear.

Arceneaux<sup>41</sup> has applied this technique to the analysis of binary mixtures of pentachlorobenzene and 1,2,3,4-tetrachlorobenzene (Fig. 17-28). Brandstatter<sup>42</sup> has applied the method to the analysis of 2,4-dinitrophenylhydrazones, Fischer and Kocher<sup>43</sup> analyzed mixtures of vanillin and ethyl vanillin.

The method is quite general, though limited to systems in which the difference in melting points is not too great. The melts must be miscible and decomposition must be absent, or at least restricted.

<sup>40</sup> Lindpaintner, Arch. Pharm., 277, 398, 1939. Reimers, Dansk. Tidsskr. Farm., 14, 219, 1940; Z. Anal. Chem., 122, 404, 1941. Dultz, Suddtsch, Deut. Apoth. Ztg., 81, 277, 1941.

<sup>41</sup> Anal. Chem., 23, 906, 1951.

<sup>42</sup> Z. physik. Chem., 191, 227, 1942.

<sup>43</sup> Mikrochemie ver. Mikrophim. Acta, 33, 131, 1946.

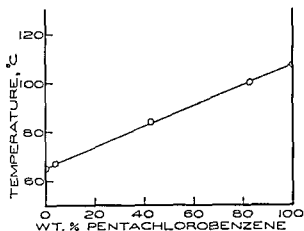


FIG. 17-28. Refractive Index Composition Relationship for Melts of 1,2,2,4-Tetrachlorobenzene and Pentachlorobenzene with Glass Powder 1.5795. (Courtesy of Claude J. Arceneaux.) Reproduced with permission from *Fusion Methods of Chemical Microscopy*, Interscience Publishers, Inc., New York, 1957.

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## Chapter 18

# QUANTITATIVE MICROCHEMICAL ANALYSIS

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## INTRODUCTION

### SCOPE

Quantitative microchemical analysis is a division of microchemistry. Microchemistry may be defined as the branch of chemical science that deals with the principles and methods for using the minimum quantity of working material to obtain the desired chemical information. The term "micro scale" has often been employed to indicate loosely that a small sample is used in a certain procedure of chemical experimentation. Since microchemistry is an extending and not a confined field, however, the sample size required will be reduced as new methods, techniques, and apparatus become available. It is more meaningful, therefore, to specify the method by the quantity of sample used. The microprocedures discussed in the present chapter require sample sizes as follows: (a) for microdetermination of the elements or molecular weight, 1 to 10 mg.; (b) for microdetermination of organic functional groups, 0.1 milli-equivalent.<sup>1</sup>

Two points should be noted when reading this chapter: first, some quantitative micromethods using smaller amounts of material have been published, albeit such procedures are still in the developmental stage; secondly, ever since the pioneer works of Emich and Pregl,<sup>2</sup> a large variety of microchemical apparatus have become commercially available. It is beyond the scope of this chapter to review the vast volume of material. The writer intends only to present simple apparatus and techniques, so that the novice can practice them without difficulty, and to discuss recent advances in the field.

<sup>1</sup> Ma, T. S., Proceedings of the International Symposium on Microchemistry 1958, Pergamon Press, London, 1959, 151.

<sup>2</sup> Emich, F., Lehrbuch der Microchemie, 2nd Ed., Bergmann, München, 1926; see Cheronis, N. D., Microchem. J., 5, 423, 1960; Pregl, F., Quantitative Organic Microanalysis, Fyfe, E., trans., Churchill, London, 1924.

THE MICROCHEMICAL BALANCE<sup>3</sup>

**Types of Microbalances.**—Microbalances suitable for quantitative analysis on the milligram scale do not differ in construction from that of the ordinary quantitative

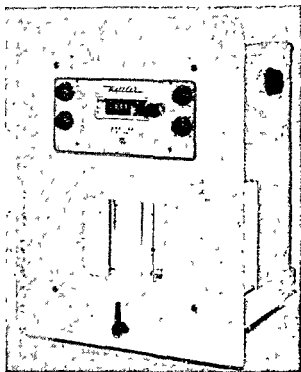


FIG. 18-1. Single-Pan Microbalance. (Courtesy Mettler Instrument Corp.)

balance. The only requirement is that the balance should have a sensitivity of about 2  $\mu$ g. (microgram) and be able to hold the load of 20 g. on each pan. The simple and rugged short-beamed Kuhlmann microbalance, which was the standard weighing device in the microchemical laboratory for several decades, went out of the market after World War II. In its place are several models having single-pan or double-pan arrangement (examples of each are shown in Fig. 18-1 and Fig. 18-2 respectively).

An excellent monograph on microbalances and microweighing has been prepared by Benedetti-Pichler.<sup>4</sup> Like the ordinary balance, the microbalance should be placed on a bench that is free from vibration. Air current around and through the microbalance should be avoided. Temperature change in the microbalance room should be minimized, and uneven heating of the different sides of

the balance should be prevented. The rules for use and care of the analytical balance are also applicable to the microbalance. Needless to say, chemicals and hot objects should never be placed directly on the balance pan, and the balance beam should be set into motion smoothly without jerking.

It is recommended to use the milligram (mg.), instead of the gram, as unit of measure for quantitative microanalysis, and record each weight to the microgram ( $\mu$ g). In the case of single-pan microbalance, the total weight of the object is indicated on the front panel. The number of milligrams and tenths of milligram are read on the left vertical scale; the marks of hundredths of milligram are read on the right scale, while the number of micrograms is estimated between two lines.

In the case of the double-pan microbalance, the number of hundredths of milligram and micrograms is shown on the pointer scale, the last figure being estimated. The pointer scale on some models has 10 lines on both sides of the center mark; on other models, 20 lines. It is advisable, however, to designate these 10 or 20 lines, respectively, as 100 pointer-scale units, so as to avoid the use of the decimal point in recording the pointer scale readings. Thus, when the microbalance is in perfect condition, moving the rider one notch (i.e., 0.1 mg.) will cause the pointer to show

<sup>3</sup> In the opinion of the writer, the microbalance should be called milligram-balance; the semimicro-balance, centigram-balance; the ordinary quantitative (analytical) balance, decigram-balance; the ultramicro-balance, microgram-balance.

<sup>4</sup> Benedetti-Pichler, A. A., *Waagen und Wagung*, in Hecht, F., and Zacherl, M. K., eds, *Handbuch der Mikrochemischen Methoden*, vol. 1, part 2, Springer, Wien, 1959.



a displacement of 100 pointer-scale units. Hence each pointer-scale unit is equivalent to one  $\mu\text{g.}$ , the lower limit of the microbalance.

As a rule, the manufacturer guarantees the new microbalance to have a sensitivity of 100, which means the displacement of exactly 100 scale units per 0.1 mg. change of weight on the pan. The sensitivity of a microbalance usually drops after

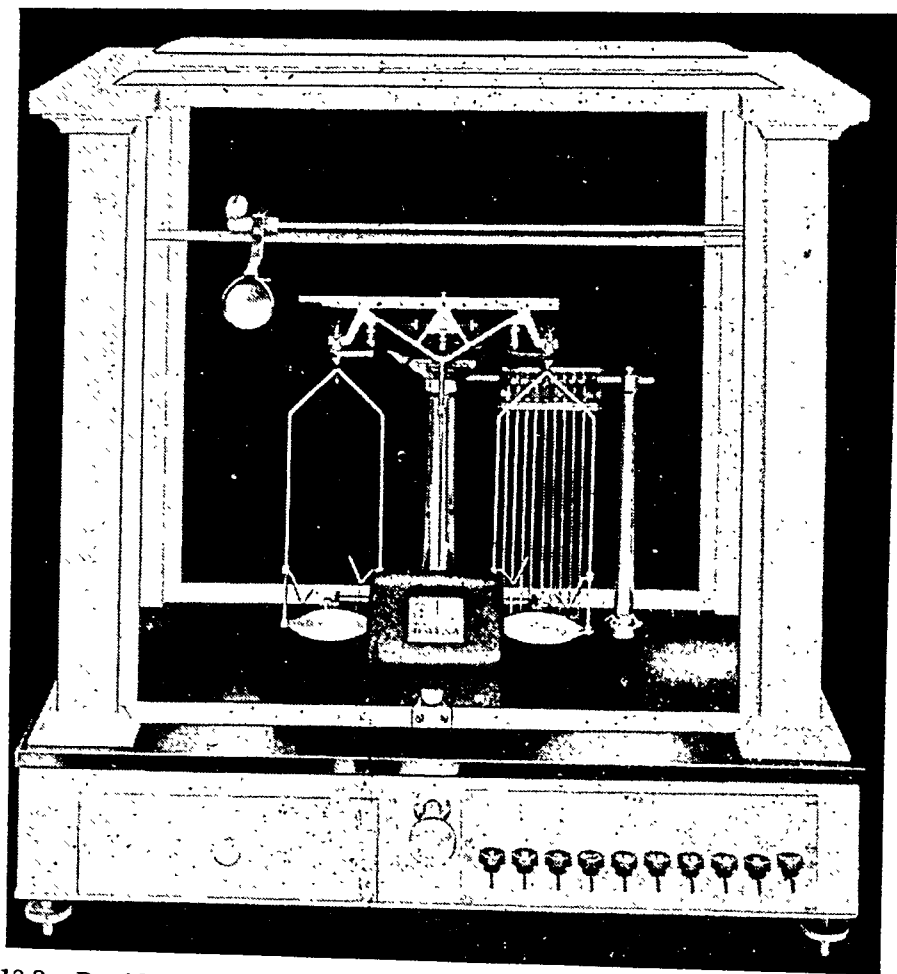


FIG. 18-2. Double-Pan Microbalance. (Courtesy William Ainsworth & Sons, Inc.)

extended use, but it should not change considerably in a year. It is not necessary to check the sensitivity of the microbalance more often than once a month. When the sensitivity is proven to be away from 100, a calibration table may be prepared to correct for the displacement in terms of scale units against micrograms. When the sensitivity drops below 80, it is advisable to reset the sensitivity by adjusting the center of gravity of the microbalance. This should be performed by an expert and not a novice who is apt to damage the microbalance.

**Weighing Technique on the Microbalance.**—The technique of operating the single-pan microbalance or the double-pan microbalance with a damping device is identical to that for the corresponding models of the ordinary analytical balance. After the object to be weighed has been carefully placed on the pan, the microbalance window is closed. The control knob is slowly turned to release the pan or pans and beam smoothly. The weights, down to the tenths of milligram, are

adjusted in the conventional manner, the balance being arrested each time when the weights are altered. Finally the balance is arrested for 20 sec. and then released to obtain the last two figures. This last step is repeated to make a check reading.

Double-pan microbalances, without the damping device, are preferably operated by means of the "swing-pair" technique to obtain the last two figures as follows. The weight is first adjusted to the nearest tenths of milligram by moving the rider. Then the balance is set in motion smoothly. Readings are taken beginning with the second swing to the right. Three or four pairs of successive inflection points of the pointer are recorded. The algebraic sum of each pair gives the "rest point" in pointer-scale units. An example is shown below.

<i>Left Swing</i>	<i>Right Swing</i>	<i>Rest Point</i>
-02	+31	+29
-01	+30	+29
00	+29	+29
+01	+29	+30

If the successive swing-pairs are erratic, improper technique or unstable condition of the microbalance during the operation is indicated, and the weighting should be repeated. The last two figures, hundredths of milligram and micrograms respectively, are obtained from the rest point and sensitivity of the microbalance.

**Tares and Fractional Weights.**—When the double-pan microbalance is employed, it is customary to prepare a suitable tare for each container used for holding the

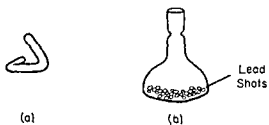


FIG. 18-3. (a) Tare Wire; (b) Tare Flask.

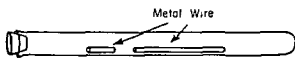


FIG. 18-4. Tare Tube.

analytical sample or the product. This eliminates the tedium of handling many pieces of weights and the arithmetic involved. Tares for containers weighing between 0.5 g. and 2 g. are conveniently made by bending copper wire into a triangular shape as shown in Fig. 18-3(a). A container that is heavier than 2 g. may be tared by means of the tare flask (Fig. 18-3(b)) or the tare tube (Fig. 18-4). The weight of the former is regulated by introducing lead shots, while that of the latter by inserting a metal wire. It is advisable to adjust the weight of the tare to about



FIG. 18-5. Fractional Weights



FIG. 18-6. Ivory Forceps for Handling Weights and Tares. (Courtesy A. H. Thomas Co)

1 mg. lighter than that of the container. Thus, some 9 mg. are left on the beam for balancing, which is adequate for weighing the sample in many cases.

The spiral form of fractional weights (Fig. 18-5) is recommended for quantitative microanalysis. The set of fractional weights ranges from 10 mg. to 500 mg., and is made of aluminum wire. It is advisable to use ivory forceps with a flat round disc at the tip (Fig. 18-6) for handling fractional weights and tares.

### PREPARATION OF SAMPLE FOR MICROANALYSIS

**Drying Device.**—When the sample submitted for quantitative microanalysis is expected to be a pure compound, it should be properly dried to remove the surface moisture, residual solvent, and solvent of crystallization, respectively. A small

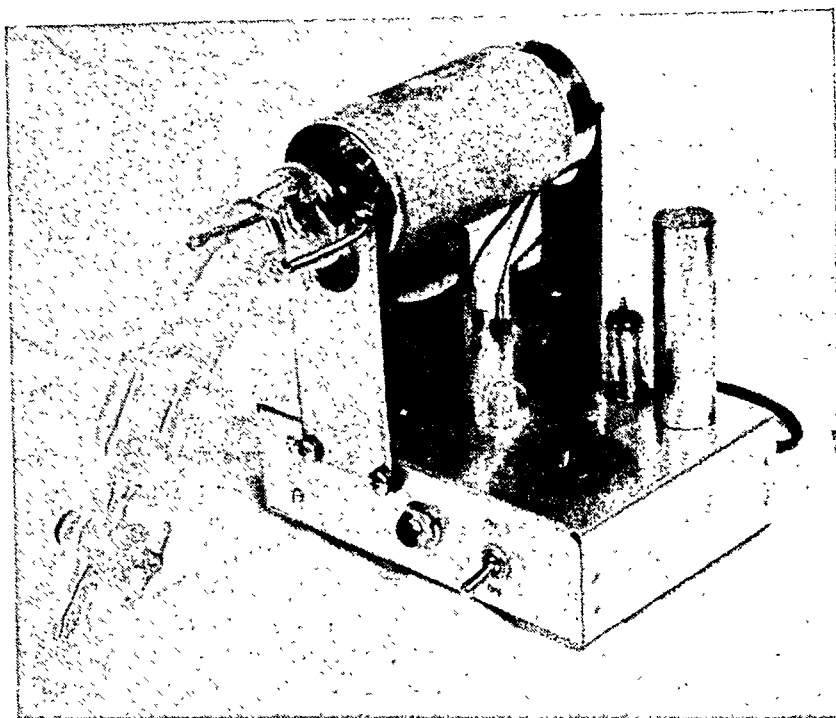


FIG. 18-7. Schenck-Ma Automatic Temperature Controlled Drying Oven. (Courtesy Micro-Ware, Inc.)

quantity of the sample is transferred into a half-dram vial. If drying at room temperature is sufficient, the vial with its contents is kept overnight in the ordinary vacuum desiccator in which phosphorus pentoxide is placed. Drying at elevated temperatures is best conducted in an automatic temperature controlled drying oven<sup>5</sup> (Fig. 18-7). Several vials containing different samples may be lined up in the large glass tube, which is inserted into a hollow aluminum cylinder heated by an external winding of resistance wire. The large glass tube is connected through a ground glass joint to the desiccant holder, which is fitted with a stopcock for evacuation. Phosphorus pentoxide is stored in a small tube that is then placed in the desiccant holder. This permits easy removal of the spent desiccant. The temperature of the drying oven is regulated by an electronic thermostat, and can be maintained between 25°C. and 300°C with a precision of  $\pm 2^\circ\text{C}$ . Thus, the sample

<sup>5</sup> Schenck, R. T. E., and Ma, T. S., *Mikrochemie*, 40, 236, 1953.

can be dried at any temperature within this range. Temperature equilibrium is reached within about 5 min. When 100 mg. or less of the sample is in the vial and the pressure is reduced to about 20 mm., the sample will be completely freed of surface moisture or solvent if the drying oven is kept at 100°C. (or the boiling point of solvent) for 1 hr.

It should be noted that samples for purity test or quality control should not be dried prior to analysis. This is also true for mixtures whose constituents are to be determined.

*Pulverizing and Mixing Devices.*—The small agate mortar and pestle (Fig. 18-8)



FIG. 18-8. Mortar and Pestle for Pulverizing Microsamples. (Courtesy A. H. Thomas Co.)

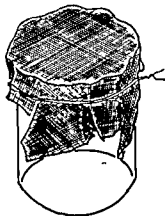


FIG. 18-9. Micro Sieve.

are used to pulverize samples that can not be broken down by cutting with the microspatula, or being pressed between two pieces of clean glass slides or glazed paper. Mixing of the pulverized product is not advisable when the analytical sample is expected to be a pure compound. On the other hand, heterogeneous samples, e.g., rocks and pharmaceutical preparations, should be finely ground and the powder sifted over a fine sieve. The latter is conveniently prepared as follows. A piece of silk-fabric or 100-mesh copper wire screen is spread over a 5-ml. beaker and the edges are then fastened by means of a rubber band or metal wire (Fig. 18-9). The powdered material is transferred onto the sieve and pushed with the microspatula. Particles which do not pass the sieve are returned to the mortar and reground. The powder in the beaker is again thoroughly mixed and a representative sample is obtained by quartering.

If a heterogeneous solid sample is completely soluble in a suitable solvent, it may be advantageous to dissolve the whole micro sample (or a relatively large weight of sample) and take aliquots for analysis. Thus, for the determination of nitrogen in fertilizer, a one-g. sample can be dissolved in water and made up to exactly 100 ml. Then 1.00-ml. portions are taken for micro-Kjeldahl determinations.

*Sample Containers.* For Solids.—The container for weighing a sample for quantitative microanalysis depends on the consistency of the sample and the determination required. Containers for handling solids include platinum, quartz, or porcelain microboats (Fig. 18-10), micro platinum or porcelain crucibles (Fig. 18-11); and glass weighing tubes (Fig. 18-12). The last item should be so fashioned that the wide end can pass through the neck of the reaction vessel used in the analysis, while the narrow end can be reached by the microspatula. The length of the handle should fit the size and shape of the reaction vessel.

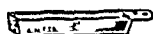


FIG. 18-10. Microboats. (Courtesy A. H. Thomas Co.)

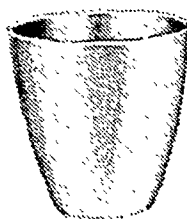


FIG. 18-11. Micro Platinum Crucible. (Courtesy Baker Platinum Division, Engelhard Industries.)

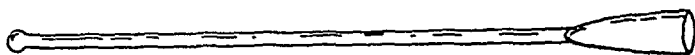
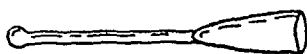


FIG. 18-12. Weighing Tube.

**For Liquids.**—Liquid samples are weighed in microweighing bottles<sup>6</sup> (Fig. 18-13) or capillaries.<sup>7</sup> The step in making the microweighing capillary is shown in Fig. 18-14. A section of capillary of about 1.5 mm. diameter, (a), is heated over a small flame until the glass softens to form a constriction, (b), with very fine channel. The flame is moved to about 15 mm. from the constriction and that

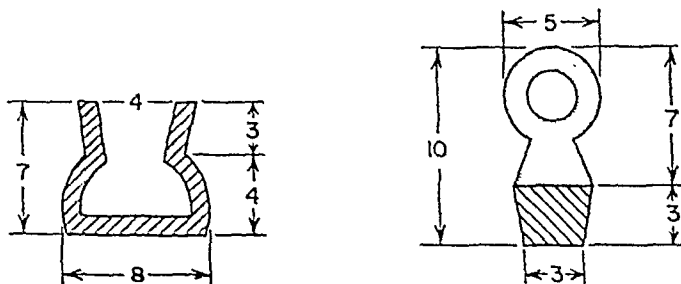


FIG. 18-13. Microweighing Bottle. (Reprinted with permission from *Microchemical Journal*, 3; 508, 1959, John Wiley and Sons, Inc.)

part of the capillary is heated until a molten section, (c), is formed. The molten glass is drawn out, (d), and broken in the flame to make a handle, (e). Then the other side of the capillary from the constriction is heated at about 25 mm., and drawn out to form a fine tip of 25 mm. length, (f). In use, the microweighing capillary is weighed on the microbalance. Then its handle is held between two fingers and the liquid chamber—between the tip and the constriction—is warmed over a tiny flame. Immediately afterwards, the tip is immersed in the liquid sample (Fig. 18-15(a)). The sample enters the capillary owing to the reduction of gas volume inside by cooling. When the liquid reaches the wide part for a length of about 2 mm., the capillary is withdrawn and the approximate increase in weight is determined. If this amount is suitable, the capillary is held by its handle, with

<sup>6</sup> Karten, B. S., and Ma, T. S., *Microchem. J.*, 3, 508, 1959.

<sup>7</sup> Ma, T. S., and Eder, K. W., *J. Chinese Chem. Soc.*, 15, 112, 1947.

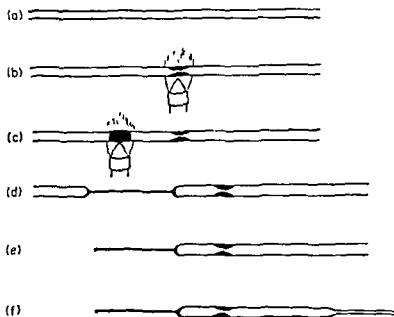


FIG. 18-14. Construction of the Microweighing Capillary.

the tip pointing upward. By gently tapping the hand holding the capillary against the other arm, the liquid will fall down the capillary until it reaches the constriction. The tip of the capillary is then sealed in the flame. The capillary containing the liquid sample (Fig. 18-15(b)) is now accurately weighed.

In case too much sample has entered the capillary, as indicated by the approximate weight, part of the sample can easily be removed by warming the lower section of the liquid chamber, whereupon the sample is pushed out, and absorbed on a filter paper. On the other hand, if more sample is desired, the entire liquid is expelled from the capillary by warming and the process of filling the capillary is repeated.

A slight modification of the filling technique described above is recommended for the liquid sample that boils near room temperature, or which consists of a mix-

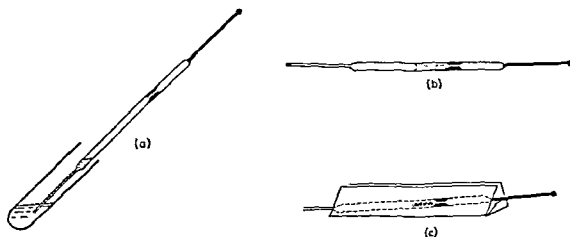


FIG. 18-15. Using the Microweighing Capillary: (a) Filling the Capillary; (b) Sealed Capillary; (c) Weighing; (c) Open Capillary Placed in Platinum Foil.

ture containing very low boiling components. Since warming the capillary is not feasible, the capillary tip is first immersed in the sample and then a piece of dry ice is caused to touch the liquid chamber. Thus, the liquid moves into the capillary because the gas inside is cooled to a temperature considerably below room temperature. Alternatively, a microweighing capillary with the tip of about 10-mm. length and 0.5-mm. bore is prepared. Then the liquid sample can be introduced to near the constriction of the capillary by means of either a dropping pipet with a fine tip or a microsyringe. As a matter of fact, these last two devices may be used for weighing liquids by difference, provided the amount taken for analysis is over 10 mg., and high precision is not required for the determination.

*Microdesiccator.*—The term microdesiccator is a misnomer since the apparatus contains no desiccant and is never used for the purpose of removing water or other solvent from the micro sample. It is just a storage device for keeping the micro-

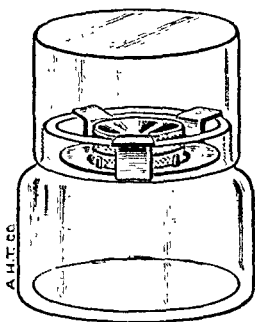


FIG. 18-16. Pregl Microdesiccator.  
(Courtesy A. H. Thomas Co.)

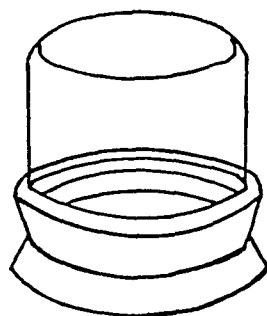


FIG. 18-17. Improved  
Microdesiccator.

boat or microcrucible holding the sample or product of analysis. It protects the material from contamination by dust, moisture, etc. in the atmosphere. It also provides a convenient means for transporting the sample from the microbalance, which is always at some distance from the site of the chemical process such as the combustion furnace or digestion stand.

The microdesiccator of Pregl (Fig. 18-16) has been displaced by other models because it is too big and clumsy. An improved design is shown in Fig. 18-17. The bottom part is a metal block cut from an aluminum or copper cylinder of 50 mm. diameter. It is machined to give a slightly concave surface depressed about 3 mm. to accommodate the top, which is a glass cover with ground glass rim. The latter is conveniently made from a 100-ml. beaker cut to a 40-mm. length, and polished. The side of the metal block is grooved so it can be held by the fingers without slipping.

As mentioned previously, under "The Microchemical Balance," a hot object should never be placed on the microbalance pan. This object should be immediately put in the microdesiccator and the glass cover replaced. Because of the efficient heat conductance of metal, a platinum microboat or microcrucible from the hot oven can be weighed after standing in the microdesiccator for 5 to 10 min., in contrast to the 30-min. minimum waiting period when porcelain plate is used in the regular desiccator for macro quantitative analysis. The microdesiccator need not be placed inside the microbalance case, and it should not be there when holding a hot object. The object to be weighed should equilibrate with the room temperature outside the microbalance.

MICRODETERMINATION OF THE ELEMENTS  
IN ORGANIC COMPOUNDS

## GENERAL

Since the largest demand of quantitative organic microanalysis is the determination of the elements, considerable attention has been given to this subject during the past two decades and a great deal of progress has been made. Now it can be said that each and every element that may be found in an organic compound can be determined by means of a reliable micromethod. Hence it is possible to make a complete analysis of any organic sample in order to account for every element that may be present. Such practice, however, is recommended only for the investigation of organic materials of completely unknown nature. For most samples, determination of one or two elements usually suffices.

A number of micromethods have been proposed in which several elements can be determined simultaneously using the same sample.<sup>8</sup> This serves to conserve the working material and save the time required for separate combustions. Precision and accuracy are often sacrificed, however, when such procedures are used.

Various automatic microcombustion assemblies have been proposed. The compact apparatus for automatic micro-Dumas determination of nitrogen, as described by Gustin,<sup>9</sup> is shown in Fig. 18-18. The operator weighs the sample and introduces it into the vertical combustion tube, then waits to read the final volume of nitrogen gas recorded on the dial. The intervening steps of sweeping, combustion, and collection of gas are carried out automatically, according to a preset time schedule. A commercial automatic microcombustion train for the determination of carbon and hydrogen is also available currently (Fig. 18-19).<sup>10</sup> The analyst needs only to weigh the sample and absorption tubes for water and carbon dioxide. The use of automatic microcombustion apparatus makes it possible for the analyst to handle several pieces of equipment at the same time. Thus, the man-hours required for each determination are reduced. Such a device is recommended for the routine microanalytical work in which a large number of samples of the same nature and approximate composition are processed. If there is a continuous variation in the nature of organic materials to be analyzed, however, the analyst should give each sample individual attention in order to avoid erratic and disappointing results.

MICRODETERMINATION OF CARBON AND HYDROGEN  
BY OXIDATION IN A COMBUSTION TUBE

**Principle.**—The micromethod described in this section is a modification of the original Pregl procedure. The organic compound is oxidized in a current of oxygen by means of copper oxide at 700° to 800°C., whereupon carbon is converted quantitatively to carbon dioxide, and hydrogen to water vapor. The respective products are then retained in suitable absorbents and weighed.

**Apparatus.**—Figure 18-20 shows the flow-sheet diagram of the microcombustion train for the determination of carbon and hydrogen. Figure 18-21 shows a com-

<sup>8</sup> See reviews by Ma, T. S., *Anal. Chem.*, **30**, 760, 1958; **32**, 80R, 1960; Ma, T. S., and Gutterson, M., *Ibid.*, **34**, 111R, 1962.

<sup>9</sup> Gustin, H. M., *Microchem. J.*, **1**, 75, 1957.

<sup>10</sup> Available from Coleman Instruments, Inc., Maywood, Ill.



mercial assembly for the same purpose. It should be noted that the preheater unit is absent in Fig. 18-20, while the nitrogen oxide-absorber is absent in Fig. 18-21. Explanations will be found in the following paragraphs, which discuss the individual parts, starting from right to left in Fig. 18-20.

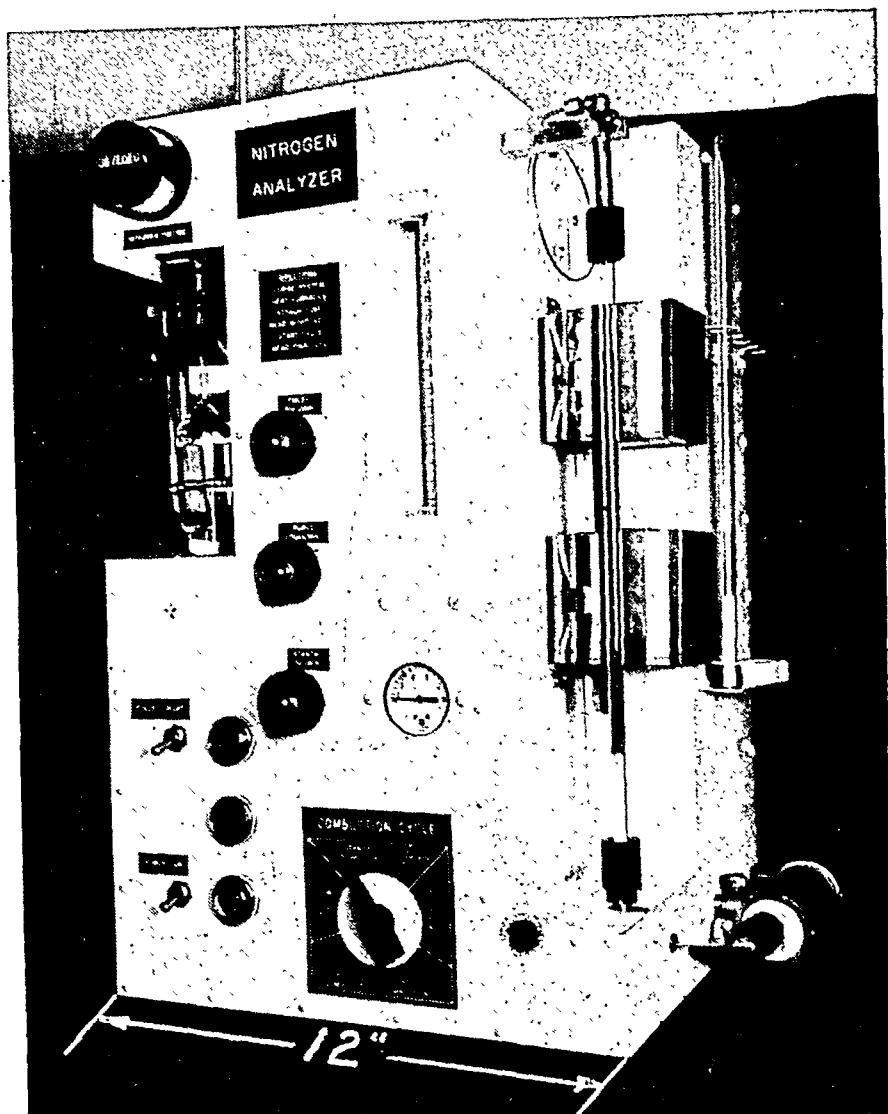


FIG. 18-18. Automatic Nitrogen Analyzer of Gustin.

**Oxygen Cylinder A.**—Oxygen of very high purity, free from hydrogen and hydrocarbons, is commercially available in large cylinders and "lecture demonstration bottles." The latter is recommended for occasional carbon and hydrogen micro-determinations. The bottle is opened gradually to regulate the flow of gas. It can also be connected to a simple regulator (Fig. 18-22). A large cylinder of oxygen, if used, should be connected with a pressure gauge and needle valve regulator. If pure oxygen is employed, blank analysis will cause negligible increase on the weights of water and carbon dioxide absorption tubes. Then, the preheater C

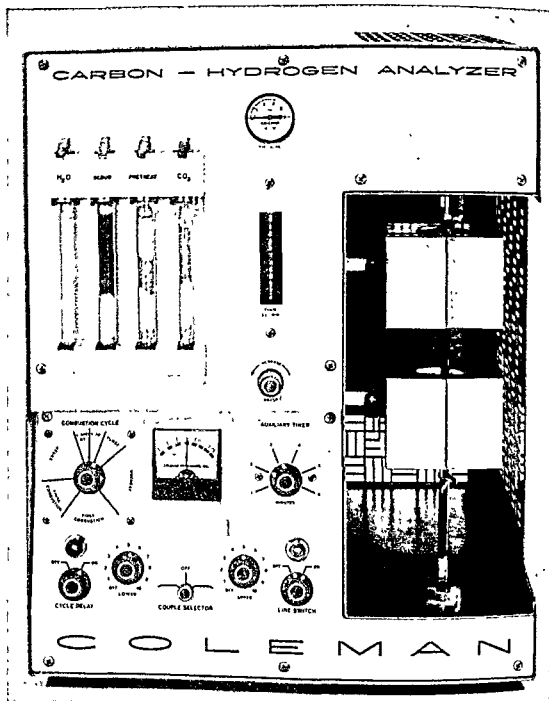


FIG. 18-19. Coleman Automatic Carbon-Hydrogen Analyzer. (Courtesy Coleman Instruments, Inc.)

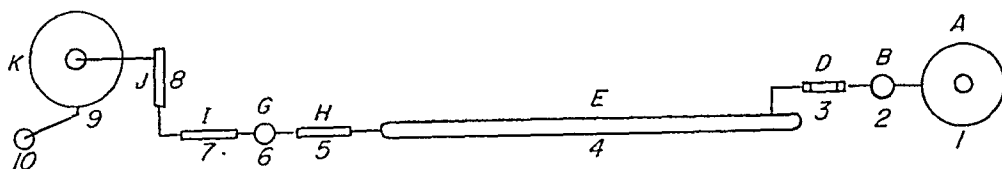


FIG. 18-20. Schematic Diagram of C-H Microcombustion Train: 1. Oxygen Cylinder; 2. Pressure Regulator; 3. Bubble Counter U-Tube; 4. Combustion Tube; 5.  $\text{H}_2\text{O}$  Absorber; 6.  $\text{N}$  Oxide Absorber; 7.  $\text{CO}_2$  Absorber; 8. Guard Tube; 9. Mariotte Bottle; 10. Graduated Cylinder.

shown in Fig. 18-21 becomes superfluous, since its purpose is to remove hydrogen and organic matter from the oxygen reservoir.

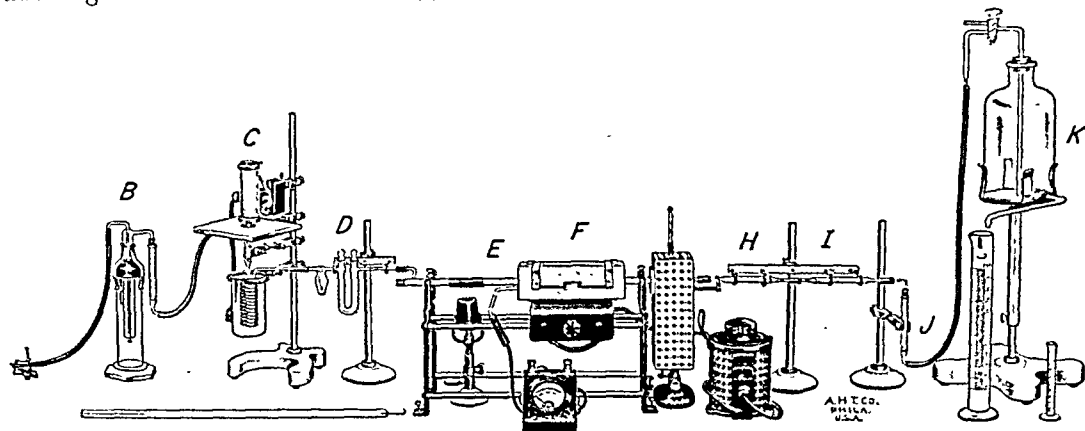


FIG. 18-21. The Carbon and Hydrogen Microcombustion Assembly Arranged for Left-Handed Operation. (Courtesy A. H. Thomas Co.)

**Constant Pressure Device B.**—The constant pressure device (Fig. 18-21 B) consists of two parts. One part is a bell jar with a central tube for gas inlet and a side arm for gas exit. The gas inlet tube should extend about 3 mm. beyond the rim of the bell jar, which is placed inside a cylinder. The latter is partially filled with distilled water to which a little sodium hydroxide is added, in order to prevent the atmospheric carbon dioxide from passing into the gas stream. When oxygen is passed into the combustion train through the pressure regulator, the water inside the bell jar will be pushed out so that the level of water surrounding the bell jar is about 60 mm. from its rim. The valve of the oxygen cylinder should be so adjusted that the bell jar is always full of gas and occasionally bubbles of oxygen escape through the outside cylinder.

**Bubble Counter—U-Tube D.**—The bubble counter is filled with concentrated sulfuric acid until the tip of the gas inlet tube is about 3 mm. immersed in the liquid. One arm of the U-tube is packed with the carbon dioxide absorbent, while the other arm, which is connected to the combustion tube, is

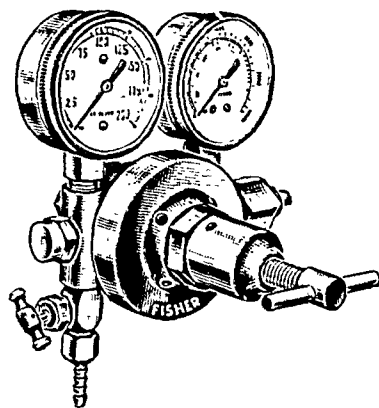


FIG. 18-22. Simple Gas Regulator. (Courtesy Fisher Scientific Co.)

filled with the water absorbent. Cotton serves as partition and as plugs at the two ends.

**The Combustion Tube E.**—A typical packing for the combustion tube for micro-determination of carbon and hydrogen is shown in Fig. 18-23. A small wad of silver thread is pushed towards the tip of the microcombustion tube, and a silver wire about 10 mm. longer than the tip is inserted through the other end. Then

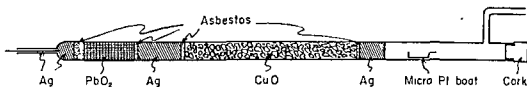


FIG. 18-23. Packing of Microcombustion Tube for C-H Analysis.

long-fibered asbestos is packed into the tube to a length of about 5 mm. This serves as a choking plug to control the speed of the gas. Lead peroxide (specially prepared for micro C-H analysis) is introduced. This section should be about 50 mm. long and should be heated at  $180 \pm 10^\circ\text{C}$ . A little asbestos is added as partition, followed by the roll of silver wire, 50 mm. long. Another asbestos partition is introduced. Then the tube is filled with the oxidizing agent, which consists of copper oxide, either in wire form or prepared from a roll of fine copper wire gauze (100 mesh) by ignition over a strong flame. This section should be about 180 mm. long, and it is followed by a little asbestos and the roll of silver wire of 40-mm. length. The length of each section should not be governed by a rigid rule but should fit the combustion furnace *F*. Electric microcombustion furnaces are commonly used nowadays, though the gas burner of Pregl (Fig. 18-24)

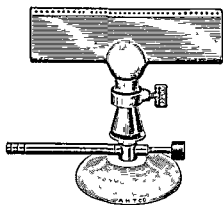


FIG. 18-24. Pregl Long Burner for Microcombustion. (Courtesy, A. H. Thomas Co.)

also gives satisfactory results. If the laboratory is air-conditioned, however, gas burners are not recommended because they generate considerable amounts of heat and carbon dioxide.

The microcombustion tube is conveniently closed with a cork stopper which fits snugly and squarely at the opening (see Fig. 18-23). The cork stopper is shaped from one that is wider than the microcombustion tube, by slowly and carefully squeezing the cork into the neck of the tube. The cork stopper is better than a rubber stopper or a ground-glass cap; if there is a sudden gas expansion inside the combustion tube, the rubber stopper or glass cap might cause an explosion.

The packing described above in this section has been called "universal packing," meaning that it may be used for the analysis of almost all types of organic compounds. It should be noted, however, that a microcombustion tube packed in this manner may not give satisfactory results for compounds containing fluorine, mercury, or osmium. Mercury and osmium tetroxide have high vapor pressure at the temperatures of combustion, and will pass into the absorption tube. Fluorine is not quantitatively retained by the silver roll; hence, a section of magnesium oxide should be incorporated into the packing.

Manganese dioxide pellets have been advocated for the removal of nitrogen oxides in place of lead peroxide. In the former case, the reagent should be placed in a tube (Fig. 18-25(a)) between the two absorption tubes as shown in Fig. 18-20 G.

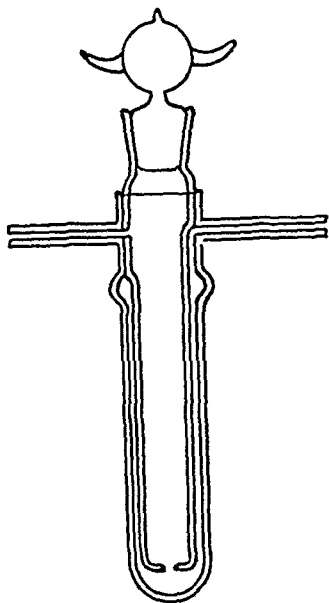


FIG. 18-25a. Absorption Tube for Removal of Nitrogen Oxides. (Courtesy A. H. Thomas Co.)



FIG. 18-25b. Absorption Tubes for Water and Carbon Dioxide. (Courtesy A. H. Thomas Co.)

The silver wire protruding from the tip of the microcombustion tube should extend into the tip of the water absorption tube (Fig. 18-20 H) so that no water drops will form in the capillary.

**Water and Carbon Dioxide Absorbers.**—These are called absorption tubes (Fig. 18-25(b)) and their dimensions should meet recognized specifications.<sup>11</sup> The water absorber is packed with Anhydrone (magnesium perchlorate dihydrate) or other suitable efficient drying agent. Cotton is used to plug both ends and form a channel as shown in Fig. 18-26. The carbon dioxide absorber (Fig. 18-20, I) is

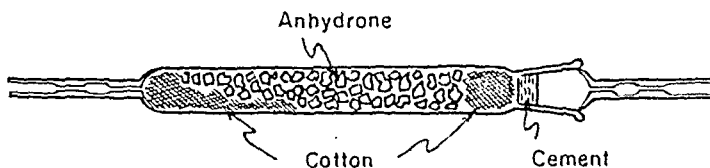


FIG. 18-26. Packing of the Water Absorber.

filled in a similar manner, except that the cotton channel is placed near the stopper and the absorption tube is first packed with a section (about 10 mm.) of Anhydrone before introducing the Ascarite (sodium hydroxide impregnated on asbestos). The stoppers are sealed by means of Kronig cement.<sup>12</sup> The stoppers of the respective absorbers should face each other in the combustion train. In order to

<sup>11</sup> U. S. Specifications recommended by the Committee on Microchemical Apparatus, Division of Analytical Chemistry, American Chemical Society; see Alber, H. K., *Mikrochemie*, 36 and 37, 75, 1951; British Standards Institution, British Standards.

<sup>12</sup> Available from A. H. Thomas Co., Philadelphia, Pa.

prevent leakage, a special kind of rubber tubing,<sup>12</sup> which is impregnated with paraffin, should be used for connections. The microcombustion tube and the respective absorption tubes should join bud-to-bud, and each pair of glass terminals should have the same outside diameter. The rubber connections should be lubricated sparingly with glycerol.

**The Guard Tube and Mariotte Bottle.**—The guard tube (Fig. 18-21, *J*) is to prevent moisture from backing up into the carbon dioxide absorber. The Mariotte bottle (Fig. 18-21, *K*) serves the purpose of varying the gas speed, if necessary, during the analysis, and measuring the volume of oxygen that has passed through the absorption tubes.

**Procedure.** Acclimatization of the Microcombustion Train.—The microcombustion train is preferably assembled on a permanent bench as shown in Fig. 18-21. Before the analysis, the valve of the oxygen cylinder is opened to pass a current of gas through the combustion and absorption tubes. The furnaces are turned on. The copper oxide section should be maintained at 700° to 800°C., while the lead peroxide and half of the silver roll should be heated at 180°C. If lead peroxide is not used, the silver roll should be kept at 300° to 400°C. Once the level of water in the pressure regulator has been adjusted so that the volume of oxygen passing through the combustion tube is about 100 ml. in 20 min. while the exit tube of the Mariotte bottle is at a horizontal position, it is not necessary to change the water in the pressure regulator for several months.

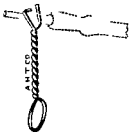


FIG. 18-27. Fork for Handling Microabsorption Tubes. (Courtesy A. H. Thomas Co)

While wearing a clean pair of gloves, the analyst checks the combustion train for leaks, by turning off the stopcock on the guard tube, so that oxygen will stop entering the bubble counter. The absorption tubes are removed from the microcombustion train and the tips of the absorption tubes are wiped with a piece of tissue paper.<sup>13</sup> The absorption tubes are placed near the microbalance for 5 min., then set on the hook of the balance pan and weighed. The tube may be handled by means of the gloved thumb and index finger, or preferably by using a special fork (Fig. 18-27). In the former case, the tube is picked up by the center section; in the latter, it is picked up by the end. The water absorption tube is weighed first, followed by the carbon dioxide absorber.

**The Course of Analysis.**—Prior to the weighing of the absorption tubes, the sample to be analyzed should be weighed. Solid substance is weighed in a platinum microboat (see Fig. 18-10); liquid sample is weighed in a capillary (see Fig. 18-15). After the absorption tubes have been replaced in the microcombustion train, the stopcock leading from the pressure regulator is turned off and the cork stopper of the combustion tube is removed.

The sample is introduced as follows: when the microboat is used as sample container, the boat is transferred from the microdesiccator (see Fig. 18-17) into the mouth of the combustion tube by means of the forceps, and then pushed inside by means of a glass or platinum wire hook until it is about 50 mm. from the silver

<sup>13</sup> The expert micro-analyst may prefer using a piece of chamois instead of the gloves and wiping the absorption tubes with wet flannel cloth and moist chamois, instead of tissue paper. The novice, however, usually finds it difficult to use this technique.

roll; if the sample is weighed in a sealed capillary, a platinum foil about 40 mm. long, bent into a triangular shape, is first placed at the neck of the combustion tube; the end of the capillary tip is cut off, and the capillary is laid on the platinum foil; the latter is pushed towards the silver roll until the capillary tip is 50 mm. away from the silver roll.

The cork stopper of the combustion tube is now replaced. The stopcock of the guard tube is then opened. If water continues to drop out from the Mariotte bottle, a leak in the system is indicated, and it should be corrected before the combustion can be started. When the train is proven to be satisfactory, the stopcock of the pressure regulator is opened. Presently bubbles should appear in the bubble counter and water should drop out from the Mariotte bottle; otherwise the micro-combustion train is clogged and should be checked.

The microboat (or platinum foil) is heated gradually by placing the burner under the combustion tube and to the right of the microboat. The burner is slowly moved leftward. Solid sample usually melts first, and then volatilizes or sublimates. Liquid sample will come out of the capillary tip and settle in the combustion tube. In order to prevent incomplete combustion, it is important to control the rate at which the sample enters the oxidizing mixture. A sample of 3 to 6 mg. ordinarily requires about 10 min.

After the sample has disappeared, 100 ml. of oxygen are passed through the microcombustion train. The stopcock of the guard tube is closed. The absorption tubes are disconnected, placed near the microbalance, and weighed as described above. The increases in weight of the respective tubes give the amounts of water and carbon dioxide produced from the sample. The respective percentages of carbon and hydrogen are then calculated.

### MICRODETERMINATION OF CARBON BY OXIDATION IN A SOLUTION

*Principle.*—The organic compound is dissolved in a phosphoric acid solution that contains such strong oxidizing agents as sulfuric, chromic, and iodic acids. Heating the reaction mixture effects the complete conversion to carbon dioxide. The latter is absorbed in sodium hydroxide solution, forming sodium carbonate. Acidification of the carbonate solution regenerates carbon dioxide gas, which is determined manometrically. The presence of nitrogen, halogens, sulfur, alkali metals, etc., does not affect the results.

This method was developed by van Slyke, Folch, and Plazin<sup>14</sup> for the microdetermination of organic materials in a solution. It can be used also for the analysis of solid samples, but it is not suitable for the determination of carbon in low-boiling liquids.

*Apparatus.*—The apparatus for microdetermination of carbon by wet combustion is shown in Fig. 18-28. The reaction vessel, *A*, is connected by means of a ball-and-socket joint to the absorption chamber assembly, *B*. The contents in the chamber can be magnetically agitated. The latter can be opened to the atmosphere through the upper stopcock, *D*, or to the mercury leveling bulb, *E*, by way of the lower stopcock, *F*.

<sup>14</sup> Van Slyke, D. D., Folch, J., and Plazin, J., *J. Biol. Chem.*, 136, 509, 1940.

**Procedure.** Preparation for the Oxidation.—The reaction vessel, *A*, is disconnected from the connecting tube. The sample is introduced into the bottom either by means of the weighing tube (see Fig. 18-12) for solids, or by using the pipet for solutions. The sample taken should contain 2 to 3 mg. of carbon. A few grains of alundum are added to act as boiling chips, and 200 mg. of potassium

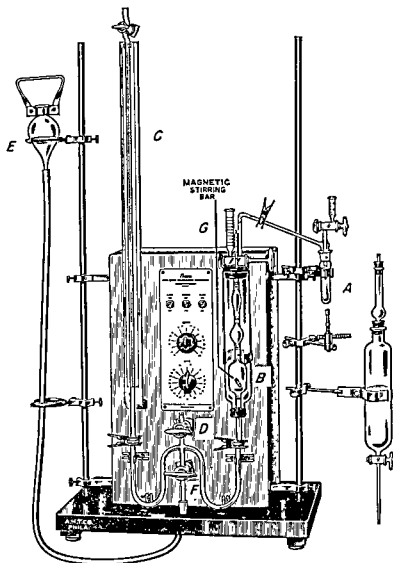


FIG. 18-28. Manometric Apparatus for Wet Combustion. (Courtesy A. H. Thomas Co)

iodate are introduced. The ground glass joint is lubricated with sirupy phosphoric acid, and the connecting tube is replaced.

The manometer is filled with mercury and its stopcock closed. With the stopcock of the reaction vessel closed, the lower stopcock, *F*, open and the leveling bulb, *E*, in the upper ring, the stopcock of the absorption chamber is carefully opened so that mercury is forced into and above the absorption chamber, *B*, until the cup of the absorption chamber assembly is filled with several milliliters of mercury. The stopcock of the absorption chamber is then closed while the lower stopcock, *F*, is left open.



Now the leveling bulb, *E*, is placed in the lower ring and the stopcock of the absorption chamber is turned so as to connect the chamber with the reaction vessel, *A*. The mercury level in the absorption chamber falls immediately since air is drawn from the reaction vessel. The leveling bulb is then lowered below the laboratory bench so that mercury is drawn out of the absorption chamber. When the mercury level in the chamber, *B*, has reached the 50-ml. mark, the lower stopcock, *F*, is closed and the leveling bulb, *E*, is returned to the upper ring of the stand. The stopcock of the absorption chamber is then closed and the lower stopcock, *F*, is again opened. This action admits mercury into the absorption chamber and compresses the trapped air. By turning the stopcock of the absorption chamber to connect the chamber to the cup, the trapped air is forced out together with a few milliliters of mercury.

A solution containing 0.5 *M* sodium hydroxide and 0.3 *M* hydrazine sulfate is introduced into the absorption chamber, *B*, in the following manner: the leveling bulb, *E*, is placed in the lower ring of the stand; the stopcocked cylinder, *G*, which holds the alkaline hydrazine solution, is fitted with a rubber tip so that the delivery end makes a gas-tight connection when the tip is pressed tightly against the bottom of the cup above the absorption chamber, which contains a few milliliters of mercury; with the stopcock on the cylinder open, the stopcock of the absorption chamber is opened slightly so that the alkaline hydrazine solution slowly enters the absorption chamber; when the hydrazine solution is about 1 mm. above the 2-ml. mark in the absorption chamber, both stopcocks are closed and the leveling bulb is returned to its holder; the stopcock of the absorption chamber is opened momentarily so that both the solution in the capillary of the cock and enough mercury for a seal are drawn into the chamber. In order to eliminate the error due to atmospheric carbon dioxide, the alkali on the walls of the cup is washed away with several portions of distilled water, each of which is removed by the water aspirator.

**The Oxidation.**—By lowering the leveling bulb, *E*, below the bench top, mercury is slowly drawn out of the absorption chamber, *B*, and the manometer, *C*. When the mercury level in the manometer stands a little below the level of the 2-ml. mark on the absorption chamber, the lower stopcock, *F*, is closed and the leveling bulb, *E*, is placed in the lower ring of the stand. The stopcock of the absorption chamber is now turned to connect the chamber with the reaction vessel, *A*. Three ml. of the oxidizing fluid (prepared by mixing 2.5 g. of chromic acid, 0.5 g. of potassium iodate, 17 ml. of sirupy phosphoric acid, and 33 ml. of fuming sulfuric acid) are introduced into the cup above the reaction vessel, *A*. The stopcock below the cup is carefully opened to allow 2 ml. of the oxidizing fluid to run into the reaction vessel, *A*, making certain that no air enters the system. The contents of the reaction vessel, *A*, are carefully heated to boiling with the microburner (or preferably in a heating stage<sup>15</sup> automatically controlled). As carbon dioxide and oxygen are evolved, the mercury falls in the absorption chamber, *B*, and rises on the manometer, *C*. During this stage, the lower stopcock, *F*, is opened momentarily every few sec. to admit mercury from the leveling bulb, *E*, into the absorption chamber, *B*, and to keep the gas space in the chamber at about 10 ml. Within 1 min. from the beginning of the heating, enough gas has been evolved to press the mercury in the manometer up to its top, and to permit the lower stopcock, *F*, to be opened completely without causing a back flow of the

<sup>15</sup> Ma, T. S., and Schenck, R. T. E., *Mikrochemie*, 40, 245, 1953.

alkaline hydrazine solution from the absorption chamber, *B*, to the reaction vessel, *A*. The lower stopcock, *F*, is now left fully open during the rest of the reflux with the system under a pressure of about 600 mm. of mercury. Vigorous boiling is continued at this pressure for 2 min. to complete the oxidation.

**Absorption of Carbon Dioxide by the Alkali in the Absorption Chamber.**—After the completion of the oxidation, the leveling bulb, *E*, is lowered below the bench top, until the level of the mercury in the absorption chamber, *B*, drops to the 50-ml. mark. The contents of the reaction vessel, *A*, boil vigorously under the reduced pressure. The leveling bulb, *E*, is quickly raised, causing mercury to return to chamber, *B*. As soon as the space in the chamber, *B*, has been compressed to about 7 ml., the leveling bulb, *E*, is quickly lowered below the bench top until the mercury in the absorption chamber falls again to the 50-ml. mark. This process of alternate expansion and compression should be repeated rapidly 25 times in about 5 min. The lower stopcock, *F*, is closed and the leveling bulb, *E*, is replaced in the lower ring of the stand.

The heater is then removed from under the reaction vessel, *A*. The stopcock of the reaction vessel is opened and the ball-and-socket joint is disconnected from the absorption chamber, *B*, the stopcock of the chamber being closed. Immediately after removal of the reaction vessel, *A*, the bent capillary tube of the stopcock above the absorption chamber must be filled with mercury. This is done by connecting the capillary through the ball joint to a test tube containing mercury, and carefully opening the stopcock, so that mercury enters the capillary and fills the cock, and a few drops fall into the absorption chamber, *B*.

**Removal of Unabsorbed Gases.** The lower stopcock, *F*, is opened and leveling bulb, *E*, is placed in the upper ring of the stand. Next the stopcock on the absorption chamber, *B*, is opened carefully, allowing the gases to escape through the mercury pool in the cup, until the alkaline hydrazine solution just reaches the bottom of the stopcock. Then the leveling bulb, *E*, is returned to the lower ring of the stand and the stopcock on the absorption chamber is opened momentarily to provide a mercury seal.

**Liberation of Carbon Dioxide and the Reading of  $P_1$ .**—A 1-ml. stopcock pipet, fitted with a rubber tip, is filled to the mark with 2 *M* lactic acid solution. The rubber tip is then pressed against the bottom of the cup above the absorption chamber, *B*, and the stopcock on the pipet is opened. By carefully turning the stopcock on the absorption chamber, *B*, exactly 1 ml. of lactic acid solution is delivered into the chamber. The pipet is removed and the stopcock on the absorption chamber is opened momentarily to effect a mercury seal. The leveling bulb, *E*, is lowered below the bench top, drawing mercury out of the absorption chamber, *B*. When the mercury reaches the 50-ml. mark in the chamber, the lower stopcock is closed and the leveling bulb is replaced in the lower ring of the stand. The magnetic stirrer is turned on and the contents of the absorption chamber, *B*, are agitated for 30 sec. Carbon dioxide is liberated causing the mercury level in the absorption chamber, *B*, to fall below the 50-ml. mark. The lower stopcock, *F*, is opened occasionally to admit some mercury into the absorption chamber, *B*, to return the mercury level at the 50-ml. mark. Finally the solution is stirred for 90 sec. to complete the reaction between sodium carbonate and lactic acid. The leveling bulb, *E*, is now placed in the upper ring in the stand and the lower stopcock, *F*, is carefully opened to force mercury into the absorption cham-

ber, *B*, until the mercury level is exactly at the 10-ml. mark. The manometer reading is then recorded. This gives the pressure  $P_1$ .

**Re-absorption of Carbon Dioxide and the Reading of  $P_2$ .**—The leveling bulb, *E*, is placed in the lower ring of the stand and the lower stopcock, *F*, is opened. One ml. of 5 *N* sodium hydroxide solution is delivered into the cup above the absorption chamber, *B*. The stopcock on the absorption chamber is carefully opened to admit the mercury in the cup into the absorption chamber. When the mercury level reaches the capillary above the stopcock, a note is made of the height of the sodium hydroxide solution in the cup, which is graduated. The stopcock of the absorption chamber is kept open until exactly 0.5 ml. of alkali have entered the absorption chamber, *B*. About 2 ml. of mercury are added to the cup and a mercury seal is again made. The excess alkali in the cup is removed by suction and rinsing with distilled water. The contents of the absorption chamber are mixed by lowering the leveling bulb, *E*, below the bench top to bring the surface of the solution down to a point a little below the 10-ml. mark, and then raising the leveling bulb to a point above the ring so that the pressure in the absorption chamber is about atmospheric, as shown on the manometer. This process of lowering and raising the leveling bulb, *E*, is repeated 3 times. Then the leveling bulb is lowered below the bench top to bring the solution meniscus in the absorption chamber, *B*, down a little below the 10-ml. mark, and the lower stopcock, *F*, is closed. The leveling bulb, *E*, is placed in the upper ring of the stand. After standing for a minute to allow complete drainage of the alkali from the walls, the lower stopcock, *F*, is carefully opened to raise the meniscus to exactly the 10-ml. mark. The manometer reading is taken, which is  $P_2$ . The temperature of the water jacket is also read.

**Calculation.**—The pressure of the carbon dioxide produced by the sample is given by the formula

$$P_{CO_2} = P_1 - P_2 - \text{blank}$$

where blank represents the pressure obtained when the entire procedure is repeated at the same temperature and using the same reagents, but without the sample. The weight in milligrams of carbon present in the sample is found by multiplying the pressure of the carbon dioxide by a factor given in Table 18-1.

$$\text{milligrams C} = P_{CO_2} \times \text{factor}$$

### MICRODETERMINATION OF NITROGEN BY THE DUMAS PRINCIPLE

**Principle.**—The Dumas method for the determination of nitrogen is based on the oxidation of the organic compound at high temperature in an atmosphere of carbon dioxide. Part of the nitrogen present in the sample is evolved as free nitrogen but most of it is converted to the oxides. The latter are reduced to free nitrogen by hot metallic copper. The gas stream is conducted through a solution of potassium hydroxide, which absorbs the carbon dioxide and other acidic gases, leaving the free nitrogen to be measured in the micro-azotometer (nitrometer).

The presence of other elements in the sample does not interfere with the Dumas method for determining nitrogen, since metallic elements will be transformed into stable solids, while volatile oxides are soluble in potassium hydroxide. It

TABLE 18-1. FACTOR FOR CARBON CALCULATION USING THE VAN SLYKE APPARATUS

Temperature, °C.	Factor × 10 <sup>3</sup>	Temperature, °C.	Factor × 10 <sup>3</sup>
15	1.437	25	1.372
16	1.430	26	1.366
17	1.424	27	1.360
18	1.417	28	1.354
19	1.410	29	1.349
20	1.403	30	1.343
21	1.397	31	1.337
22	1.390	32	1.332
23	1.384	33	1.327
24	1.378	34	1.321

should be noted, however, that complete conversion of the carbon to carbon dioxide in the sample is essential for this analysis. Methane and carbon tetrahalides, especially carbon tetrafluoride, are resistant to oxidation. If these compounds escape into the micro azotometer, the results of nitrogen determination will be affected.

**Apparatus.**—The micro-Dumas combustion train may be assembled in various ways. The ASTM standard form<sup>16</sup> is shown in Fig. 18-29, arranged for use in left hand position. It consists of the gasometer assembly, *A*, which is connected to a source of carbon dioxide; the Z shaped connecting tube, *B*; microcombustion tube, *C*, which is heated by 2 electric furnaces; 3-way stopcock, *D*; and micro azotometer, *E*, which is connected to the leveling bulb, *F*. The gasometer assembly, *A*, is incorporated for the purpose of measuring the volume of carbon dioxide led to the combustion tube. This can be advantageously eliminated. If the source of carbon dioxide is not pure, however, the gasometer should be used with a correction factor proportional to the volume of gas consumed.

**Carbon Dioxide Generator.**—When dry ice (solid carbon dioxide), free from air, is available, a simple carbon dioxide generator is prepared from a thermos bottle fitted with a rubber stopper and gas pressure relief valve<sup>17</sup> (Fig. 18-30). The bottle is filled with crushed dry ice and the stopper, with a mercury valve, is put in place. Pressure will be built up, and it is quickly released by opening the stopcock. This process is repeated several times to expel all the air trapped in the bottle. The generator is then ready for use. One filling will keep for about 3 days, and supplies enough carbon dioxide for about 10 microdeterminations.

A modified Poth generator, shown in Fig. 18-31, is recommended for routine analysis. The apparatus consists of 2 connecting bulbs in an atmosphere of carbon dioxide under a pressure about 20 mm. mercury higher than atmospheric. A con-

<sup>16</sup> ASTM Specification E1148-59 T.

<sup>17</sup> Steyermark, A., et al., Anal. Chem., 21, 1560, 1949.

concentrated solution of potassium bicarbonate is placed in the upper bulb, while the lower bulb holds sulfuric acid (50%). After the apparatus has been properly filled,<sup>18</sup> the system is permanently free from air and will last for several hundred microdeterminations.

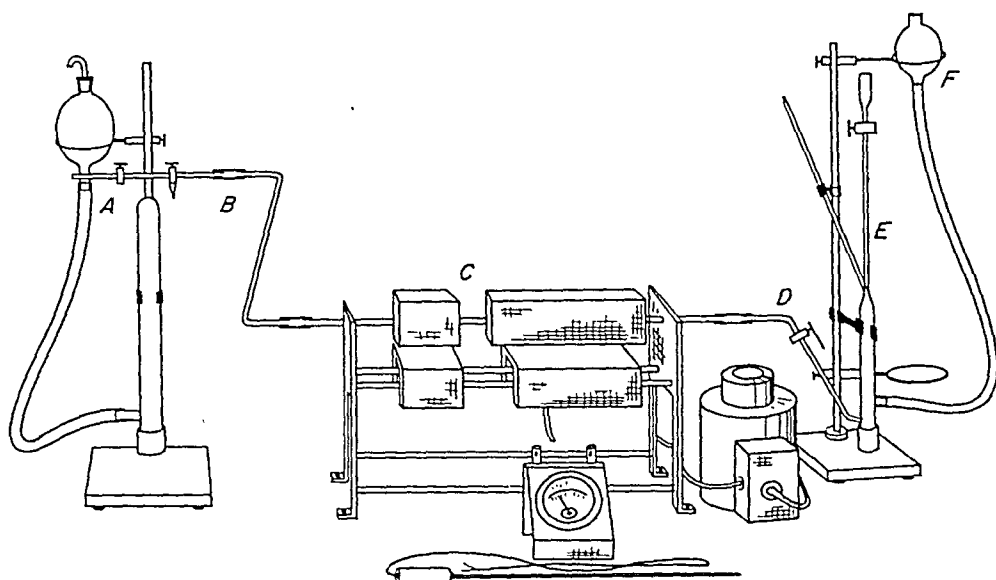


FIG. 18-29. Microcombustion Train for Dumas Nitrogen Analysis. (Courtesy A. H. Thomas Co.)

**Micro Azotometer and Connecting Stopcock.**—The micro azotometer has a capacity of 1.5 ml. and is graduated in 0.01 ml. The volume of nitrogen gas collected is estimated to the thousandth of a millimeter by the aid of a magnifying glass. A 3-way stopcock connected to the azotometer by ball-and-socket joint is specified in the ASTM Standard form (see Fig. 18-29). A two-way stopcock with long handle, however, is easier to operate, and the stopcock is preferably sealed to the micro azotometer in order to prevent leakage through the joint. Small tapered grooves should be cut in the plug of the stopcock to facilitate accurate gas flow adjustment.

**Heating Devices.**—If electric furnaces are used, as shown in Fig. 18-29, both furnaces should be of the type that can be opened up and retracted away from the microcombustion tube. The 2 furnaces should be connected to separate variable resistors so that the long furnace is maintained at a temperature of 700° to 800°C., while the short furnace can be regulated from 250° to 900°C. In the absence of electric furnaces, the short furnace can be replaced by a Bunsen burner, and the long furnace by a Pregl long burner (see Fig. 18-24).

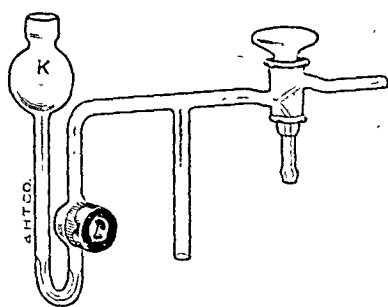


FIG. 18-30. Gas Pressure Relief Valve. (Courtesy A. H. Thomas Co.)

<sup>18</sup> Poth, E., Ind. Eng. Chem., Anal. Ed., 3, 202, 1931.

*Procedure.* Assembling the Microcombustion Train.—The micro azotometer, (Fig. 18-29) is filled with mercury up to a level about 3 mm. above the side arm joined to the stopcock. A pinch of mercuric oxide (made by heating mercuric chloride in a small test tube) is added, together with a 10-mm. headless iron na-

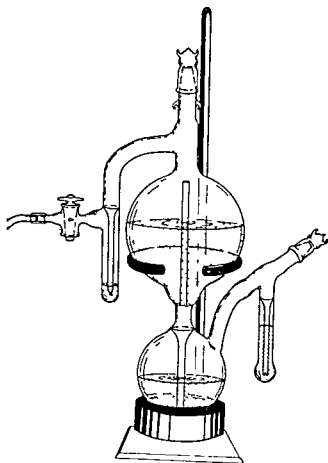


FIG. 18 31. Modified Poth Carbon Dioxide Generator.

The former provides a rough surface so that the gas bubbles do not accumulate at the bottom, while the latter can be brought up to the top (by using a magnet) to break up any foam on the surface of the potassium hydroxide solution. A cold concentrated solution of potassium hydroxide (1:1 by weight) is poured through the leveling bulb, *F*, so that the liquid level extends about 10 mm. inside the cup on top of the micro azotometer, *E*, and also beyond the rubber tubing of the leveling bulb, *F*.

The micro azotometer is connected to the tip of the microcombustion tube, *C* (after being packed as described below), by means of a 30-mm. long special rubber tubing, which is impregnated with paraffin. The wide end of the microcombustion tube is then connected to the source of carbon dioxide through the Z-shaped connecting tube, *B*.

*Packing the Microcombustion Tube.*—A small ball of silver thread is pushed to the tip of the microcombustion tube to serve as a plug. With the microcombustion tube in a vertical position, copper oxide (wire form) is poured through

a funnel. The funnel (see Fig. 18-32) should have a smooth constriction so that the material can be poured down readily. The first section of copper wires should extend 50 mm. beyond the long furnace and also 50 mm. within it. A little long-fiber asbestos is introduced to serve as partition. Then a roll of 100-mesh copper gauze,<sup>19</sup> wrapped around a heavy copper wire 50 mm. long and fitting the combustion tube snugly, is inserted and pushed towards the asbestos. After putting in another partition of asbestos, copper oxide wires are again introduced into the tube until they reach the edge of the long furnace. This portion of the packing is called the "permanent filling,"<sup>20</sup> which need not be changed for at least 100 microdeterminations, unless the copper gauze roll is oxidized by mishandling. The 2 sections of copper oxide wires in the permanent filling may be replaced by copper oxide gauze rolls, prepared by heating rolls of 100-mesh copper gauze of suitable length over a strong flame. Wires are more convenient to use, however. The "permanent filling" is separated from the "temporary filling" by a layer of asbestos.

**The Course of Analysis.**—If the sample subjected to micro-Dumas analysis is a solid, it is weighed by means of the microweighing tube (Fig. 18-12) and then placed into a mixing tube (Fig. 18-33), which is fitted with either a good cork stopper or a ground-glass cap. The microcombustion tube is held in the vertical position after the "temporary filling" (the portion beyond the "permanent filling") has been removed, and the funnel is inserted. A 50-mm. section of copper oxide wires is introduced, followed by 10 mm. of fine copper oxide. Now the sample in the mixing tube is covered by a 10-mm. layer of fine copper oxide. The stopper is replaced and the contents in the tube are shaken to mix the sample with fine copper oxide. The mixing tube is tapped gently to bring down the powder which might have stuck to the stopper. The stopper is now removed and the contents of the mixing tube are poured through the funnel into the microcombustion tube. Two small portions of fine copper oxide are added to the mixing tube, which is shaken, and its contents then poured into the microcombustion tube. Then a 50-mm. section of copper oxide wires is put on top of the fine copper oxide, and the microcombustion tube is replaced on the combustion stand.

If the sample is an oil, it is weighed in a microboat (Fig. 18-10). The direction

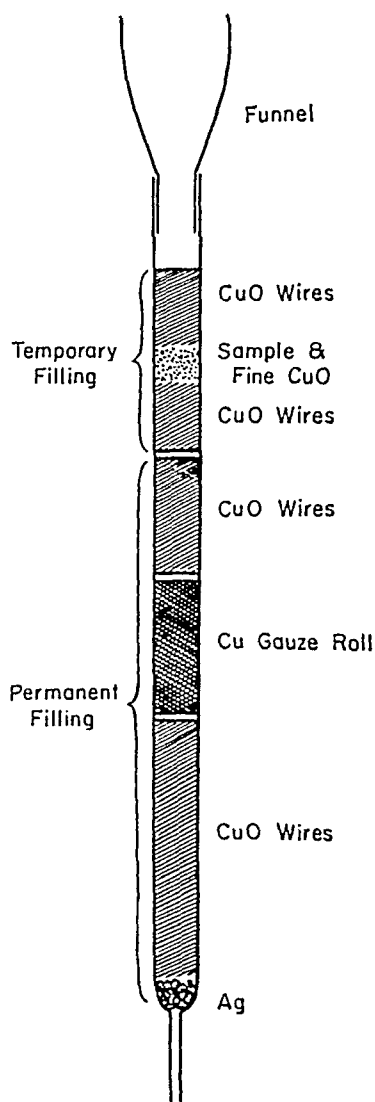


FIG. 18-32. Packing the Micro-Dumas Combustion Tube for a Solid Sample.

<sup>19</sup> Available from Fisher Scientific Co., New York, N. Y.

<sup>20</sup> Roth, H., *Quantitative Organic Microanalysis of Fritz Pregl*, Dow, E. B., trans., Blakiston, Philadelphia, 1937.

for introducing the microboat and its contents into the combustion tube is given in the next paragraph.

NOTE.—Some micro-analysts also use the microboat to hold solid sample for micro-Dumas determination. The mixing tube technique, however, provides intimate contact of the organic substance with copper oxide. It gives better results except for compounds which are decomposed on shaking with copper oxide, liberating nitrogen.

A volatile liquid is weighed in the weighing capillary (Fig. 18-15). After the oil or liquid sample has been weighed out, the microcombustion tube is removed from the stand. The temporary filling is emptied out, a 50-mm. section of copper oxide wire is introduced, followed by 20 mm. of fine copper oxide, and the microcombustion tube is replaced on the stand. When the microboat is used, the boat containing the sample is placed at the neck of the microcombustion tube and is carefully pushed towards the fine copper oxide. When the capillary is employed, a roll of copper oxide gauze with a 2-mm. bore is placed at the neck of the microcombustion tube. The tip of the capillary is cut and the capillary is inserted into the copper oxide gauze roll. The combustion tube is then held at a vertical position and fine copper oxide is introduced until the microboat (or copper oxide gauze with the weighing capillary) is covered with it. Then a 50-mm. section of copper oxide wire is added, and the combustion tube is replaced on the stand.

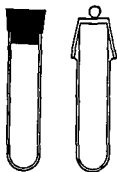


FIG. 18-33. Mixing Tube

The neck of the microcombustion tube, which is packed with the sample, is then cleaned with a wad of cotton. The rubber stopper (without the Z-shaped connecting tube, *B*) is lubricated with a trace of glycerol and inserted into the combustion tube. Then the paraffin-impregnated rubber connection is sparingly lubricated and the tips of the combustion tube and stopcock, *D*, are joined glass-to-glass. Finally the Z-shaped connecting tube, *B*, is inserted through the hole of the rubber stopper until the tapered end of the connecting tube, *B*, protrudes about 2 mm. beyond the rubber stopper.

With the leveling bulb, *F*, placed in the lower ring, and the stopcocks of the micro azotometer opened, a rapid current of carbon dioxide is passed through the microcombustion train to displace all the air in the system. After 3 min., the stopcock, *D*, of the azotometer is closed and then turned carefully to allow gas bubbles to enter the azotometer slowly. If the bubbles disappear on reaching the top of the azotometer, the system is completely free of air. Now the carbon dioxide source is turned off, and the stopcock, *D*, is closed. The stopcock on top of the azotometer is opened while the leveling bulb, *F*, is raised to bring some potassium hydroxide solution into the cup above the azotometer, and then closed. The leveling bulb, *F*, is placed in the lower ring. The stopcock, *D*, with a long handle is slowly opened, whereupon bubbles enter the azotometer but should be completely absorbed.

The short furnace is placed near the neck of the microcombustion tube in a position about 20 mm. from the sample. While the "permanent filling" is heated at 700° to 800°C. by the long furnace, the temperature of the short furnace is gradually raised to 700°C. Expansion of the gas volume in the combustion tube on heating will cause bubbles to enter the azotometer. The short furnace is now slowly advanced towards the sample. As the sample vaporizes and is oxidized, a



slow but steady stream of gas bubbles will enter the azotometer. This process should be continued until the short burner meets the long burner. Then the stopcock, *D*, is closed and, after the source of carbon dioxide has been turned on, very carefully reopened so that bubbles enter the azotometer at the rate of 2 bubbles per sec. Nitrogen produced from the sample is carried into the azotometer and rises to the top. The short burner is now moved back to near the neck and advanced once more towards the long furnace in the course of 5 min. Then both furnaces are turned off.

When all bubbles entering the azotometer are completely absorbed, the nitrogen in the combustion train is all driven into the azotometer. The stopcock, *D*, is closed and the leveling bulb, *F*, is placed in such a position that the meniscus of liquid in the bulb is at the same level as that in the azotometer. After 5 min., the volume of nitrogen is read with the aid of the magnifier, and the barometer and thermometer readings are noted. If a little liquid adheres to the tip of the azotometer below the stopcock, it can be pushed into the cup by holding the leveling bulb, *F*, above the cup and carefully opening the stopcock. If a foam is formed on the surface of the potassium hydroxide solution, it can be removed by guiding the iron nail on the mercury upward with a magnet and moving the nail up and down the foam. The volume of nitrogen is read again after such adjustments.

The microcombustion tube should be kept in the train until it has cooled down to room temperature. If another determination is not to follow, it is not advisable to empty the temporary filling, as this will introduce air into the system. On the other hand, the level of potassium hydroxide solution should be brought down below the graduated portion of the azotometer, and the stopcock below the cup should be protected from danger of being frozen.

**Calculation of the Result.**—The volume of nitrogen measured in the micro-azotometer requires a correction factor for several reasons: (1) the azotometer is calibrated against mercury and not concentrated potassium hydroxide solution; (2) there is a film of alkali on the narrow walls of the azotometer; (3) the alkali solution exerts significant vapor pressure. Pregl proposed to deduct 2% of the measured volume, while Niederl and Niederl<sup>21</sup> recommended a 1% deduction plus a blank correction. A more accurate method is to calibrate the micro-azotometer against a known nitrogen compound of the highest purity, such as the microchemical standards supplied by the Bureau of Standards.

The weight of nitrogen obtained from the sample can be calculated from the corrected volume, temperature, pressure, and the atomic weight of nitrogen. Niederl and Niederl<sup>21</sup> have prepared a nitrogen reduction table that gives the logarithm of the weight of 1 ml. of nitrogen at a given temperature and pressure.

## MICRODETERMINATION OF NITROGEN BY THE KJELDAHL PRINCIPLE

**Principle.**—When a compound containing aminoid nitrogen is heated with concentrated sulfuric acid, the organic molecule is decomposed and nitrogen is converted to ammonium sulfate. The reaction is catalyzed by the presence of certain metals, e.g., selenium, copper, mercury, etc., and facilitated by raising the reflux temperature through the addition of potassium sulfate. Some non-aminoid com-

<sup>21</sup> Niederl, J. B., and Niederl, V., *Micromethods of Quantitative Organic Analysis*, John Wiley and Sons, Inc., New York, 1938.

pounds such as nitro and nitroso compounds can be analyzed by the micro-Kjeldahl method after being subjected to reduction with zinc and hydrochloric acid prior to sulfuric acid digestion.<sup>22</sup>

After the quantitative conversion of organic nitrogen to ammonium sulfate, the reaction mixture is transferred to a distilling apparatus where sodium hydroxide is added to liberate ammonia. The latter is conveniently absorbed in boric acid solution and determined by titration with standardized 0.01 *N* acid solution.<sup>23</sup>

**Apparatus.**—Micro-Kjeldahl digestion flasks, stands, and distilling assemblies are available commercially in various forms. The apparatus described below are simple and can be easily constructed.

**Digestion Flasks.**—These can be made from ordinary 150-mm. (6-in.) borosilicate test tubes with the bottom blown out to form a bulb of about 25-mm. diameter and 6-ml. capacity. A larger bulb is required when the pre-reduction step is incorporated.

**Digestion Stand.**—A digestion stand for 6 flasks is made from a Transite board, 10 by 35 cm., with 6 holes of 22-mm. diameter drilled in it. The board is set on a metal frame with four legs 10 cm. high. A heavy copper wire supports the necks of the digestion flasks. The burner is made from a Bunsen burner with its tube replaced by copper tubing 35 cm. long. Six holes, about 1 mm. in diameter, are drilled along the copper tubing, 2.5 cm. below the holes of the Transite board. The first hole should be about 6 cm. away from the air screw of the burner. If the digestion is not carried out in the hood, a fume duct,<sup>24</sup> which is connected to the water tap through a glass aspirator, is added to the stand.

**Distillation Apparatus.**—As shown in Fig. 18-34, this is made of borosilicate glass, and is built in 2 compact units joined glass-to-glass by means of a short rubber tubing, *B*. The whole apparatus is conveniently clamped onto an iron stand and occupies a desk space of 30 by 40 cm. The steam generator, *A*, is made from a 1-liter round-bottomed flask to which a side arm is attached for refilling. When it is two-thirds filled with distilled water, before distillation is begun, enough steam will be generated for 8 to 12 determinations.

**Procedure. Digestion for Amino Compounds.**—A 2- to 5-mg. sample, containing 0.2 to 1 mg. of nitrogen, is accurately weighed and transferred into the bottom of the digestion flask. A long-handled weighing tube (Fig. 18-12) is used for weighing solid samples; a porcelain microboat (Coors, size 5 zeroes) is employed for weighing semi-solids and heavy oils, and is slid into the digestion flask. About 5 mg. of powdered selenium (mercuric oxide is used for pyridine type compounds) and 20 mg. of copper sulfate-potassium sulfate mixture (1:1) are added, followed by 1 ml. of concentrated sulfuric acid. When a large volume of the sample is taken, as in the case of biological fluids and dilute solutions, it is better to acidify the sample (after introduction into the digestion flask) with a drop of sulfuric acid, and concentrate the volume to less than 1 ml. before adding the catalyst and 1 ml. of concentrated sulfuric acid.

The digestion flask is placed on the digestion stand and the reaction mixture is boiled gently with a flame about 2 cm. high. The reaction is usually complete in 10 min. After cooling, 2 ml. of distilled water are added, and the solution is again cooled.

<sup>22</sup> Ma, T. S., Lang, R. E., and McKinley, J. D., Jr., *Mikrochim. Acta*, 1957, 368.

<sup>23</sup> Ma, T. S., and Zuazaga, G., *Ind. Eng. Chem., Anal. Ed.*, 14, 280, 1942.

<sup>24</sup> Niederl, J. B., and Niederl, V., *Micromethods of Quantitative Organic Analysis*, John Wiley and Sons, Inc., New York, 51, 1938.

**Reduction and Digestion of Nitro Compounds.**—Between 3 to 8 mg. of the compound, corresponding to about 0.5 mg. nitrogen, is weighed into the bottom of a 30-ml. micro-Kjeldahl digestion flask. One ml. of glacial acetic acid is added to dissolve the sample and the flask is warmed, if necessary, to effect solution. Upon cooling, 100 mg. of zinc powder are introduced, followed by 1.5 ml. of methanol. Then 2 drops of concentrated hydrochloric acid are added to generate hydrogen smoothly. When the evolution of gases slows down, more hydrochloric

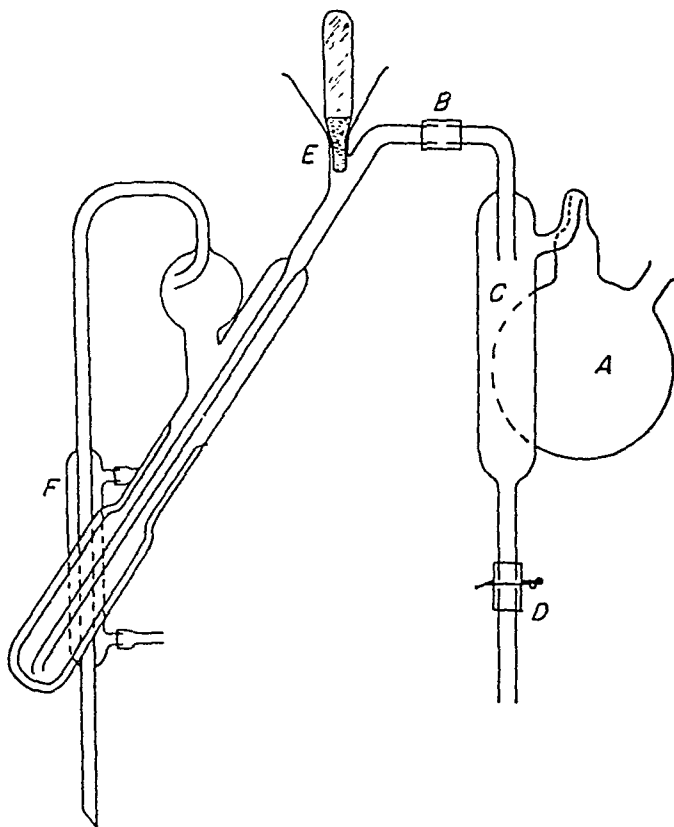


FIG. 18-34. Micro-Kjeldahl Distillation Apparatus.

acid is introduced. Toward the end, the flask is heated over a small flame to keep the evolution of hydrogen proceeding smoothly. Two drops of concentrated sulfuric acid are then added, and the reaction mixture is gently boiled to remove the volatile solvents (but not to dryness). Upon cooling, 1.5 ml. of concentrated sulfuric acid are added and the flask is again heated until the solution darkens. The reaction mixture is then cooled, 700 mg. of potassium sulfate and 25 mg. of selenium powder are added, followed by 0.5 ml. of concentrated sulfuric acid. The reaction mixture is now digested by boiling gently for 1 hr. The contents of the digestion flask are then allowed to cool. Before the reaction mixture completely solidifies, 3 ml. of distilled water are carefully introduced along the wall of the flask.

**Distillation and Titration.**—The distilled water in the steam generator, *A*, is boiled with a flame from the Bunsen burner about 10 cm. high, the ground glass plug of funnel, *E*, being placed in position and pinch clamp, *D*, closed. The rate

of distillation should be about 5 ml. per min. Then the burner is removed from under the steam generator, *A*, whereupon the condensate in the distilling flask, *G*, is sucked back into the steam trap, *C*. The funnel, *E*, is filled with distilled water and the stopper is momentarily lifted up to drain the water into the distilling flask, *G*. The burner is now replaced under the steam generator for about 20 sec. and again removed. Meanwhile 5 ml. of 2% boric acid solution and 0.05 ml. of methyl red-bromocresol green mixed indicator (1:5) are delivered into a 50-ml. borosilicate Erlenmeyer flask.

When the distilling flask, *G*, has been emptied, the Bunsen burner is replaced under the steam generator, *A*, and the pinch clamp, *D*, is opened to remove liquid from the steam trap, *C*. The pinch clamp is left on the glass tubing, through which the steam escapes. The Erlenmeyer flask containing boric acid is then placed under the condenser and supported in an oblique position so that the tip of the condenser is completely immersed in the liquid.

A trace of vaseline is smeared on the lip of the digestion flask to prevent the contents of the flask from dripping down outside. The ground-glass plug of the funnel, *E*, is removed, and the contents of the digestion flask is poured into the distilling flask, *G*. The digestion flask is quickly rinsed twice with 2-ml. portions of distilled water, and the rinsings are poured into the distilling flask. Then a suitable volume (8 ml. for amino compounds; 15 ml. for nitro compounds) of 30% sodium hydroxide solution (a little sodium thiosulfate should be added when mercury is used as catalyst) is added into the distilling flask, *G*, through the funnel, *E*, and the ground-glass plug is replaced. The pinch clamp, *D*, is replaced on the rubber tubing, whereupon steam enters the distilling flask, *G*, and stirs up its contents. Ammonia is liberated and escapes with steam through the condenser into the boric acid solution.

The boric acid solution changes from bluish purple to bluish green as soon as it comes into contact with ammonia. One min. after the boric acid has changed color, the Erlenmeyer flask is lowered so that the condenser tip is 10 mm. above the liquid. While the end of the condenser is washed with a little distilled water, the distillation is continued for another min. The burner is removed and the ammonia in the Erlenmeyer flask is titrated with standardized 0.01 *N* hydrochloric acid or potassium biniodate until the blue color disappears. (If preferred, the titration may be continued until a faint pink tinge appears; 0.02 ml. are then subtracted from the buret reading. There is no danger in missing the end point, because after the pink color appears, the intensity of pink color increases tremendously with a trace more of the 0.01 *N* acid.)

### MICRODETERMINATION OF OXYGEN

**Principle.**—Unterzaucher<sup>25</sup> proposed a method for the microdetermination of oxygen which involves pyrolysis of the organic substance over a large excess of carbon in a stream of nitrogen. The combustion furnace is heated at  $1120^{\circ} \pm 10^{\circ}\text{C}$ . because both carbon dioxide and water react with carbon quantitatively to form carbon monoxide at this temperature range. (It has been confirmed,<sup>26</sup> however, that the furnace temperature can be reduced to  $850^{\circ}\text{C}$ . when platinized carbon is used.) The carbon monoxide, after leaving the combustion furnace, is oxidized to carbon dioxide by iodine pentoxide at  $110^{\circ}\text{C}$ ., whereupon an equivalent amount

<sup>25</sup> Unterzaucher, J., *Berichte*, 73B, 391, 1940.

<sup>26</sup> Pansare, V. S., and Mulay, V. N., *Mikrochim. Acta*, 1961, 606.

of iodine is liberated. The latter is determined by titration with 0.01 *N* sodium thiosulfate.

**Apparatus.**—The commercial assembly, which is based on the design of Aluisse and co-workers,<sup>27</sup> is shown in Fig. 18-35. The schematic diagram as given by Steyermark is shown in Fig. 18-36,<sup>28</sup> the apparatus being arranged for left hand operation.

**Procedure.**<sup>27, 28</sup>—The sample, containing about 1 mg. of oxygen, is weighed in a platinum boat or glass capillary as in carbon and hydrogen determinations (p. 372). A current of pure nitrogen is conducted through the system at the rate of 10 ml. per min. The 3-way stopcocks, *H* and *H'*, at the ends of the combustion tube, *G*, are turned so that nitrogen is passed in the reverse direction through *G*, and out through the stopcock of the cap, *F*. The cap, *F*, is removed and the sample is

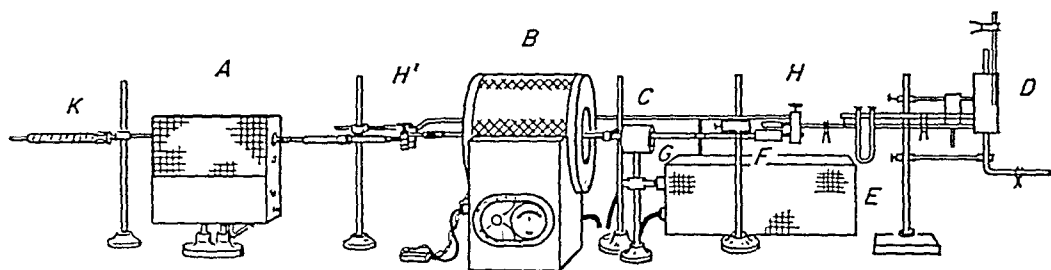


FIG. 18-35. Assembly for Microdetermination of Oxygen. (Courtesy A. H. Thomas Co.)

introduced and pushed to within about 8 cm. of the long furnace kept at 1120°C. The cap, *F*, is immediately replaced, its stopcock being left open. The reverse flow of nitrogen through the combustion tube, *G*, and out through the cap, *F*, is continued for 20 min. in order to expel all of the air that entered the system during the insertion of the sample.

The inner walls of absorption tube, *K*, are moistened with 20% sodium hydroxide solution by sucking up the alkali through the tip and draining. The absorption tube is then joined to the oxidation tube (filled with iodine pentoxide) and the Mariotte bottle as shown in Fig. 18-36. The stopcock of the cap, *F*, is now closed and the 3-way stopcocks, *H* and *H'*, are turned to let nitrogen enter the combustion tube, *G*, through its side arm, and pass into the oxidation tube.

The short movable furnace is heated to about 1120°C. and gradually brought up towards the sample until it touches the long furnace in about 30 min. The short furnace is moved back and a strong burner is played on the section of the combustion tube which was between the two furnaces. This insures complete pyrolysis of any material which may have condensed in the cooler portion of the tube. The short furnace is allowed to cool, after which the stream of nitrogen is continued until 700 ml. of gases pass through the system during the course of the determination. The stopcock of the Mariotte bottle is closed. The absorption tube, *K*, is disconnected and its contents are carefully rinsed with 125 ml. of distilled water into a 250-ml. iodine flask containing 10 drops of bromine and 10 ml. of 10% potassium acetate in glacial acetic acid. The stopper of the iodine flask is replaced and the contents are mixed. Then 10 ml. of 20% sodium acetate solution is added.

<sup>27</sup> Aluisse, V. A., Hall, R. R., Staats, F. C., and Becker, W. W., *Anal. Chem.*, 19, 347, 1947.

<sup>28</sup> Steyermark, A., *Quantitative Organic Microanalysis*, 2nd Ed., Academic Press, New York, 1961, 380.

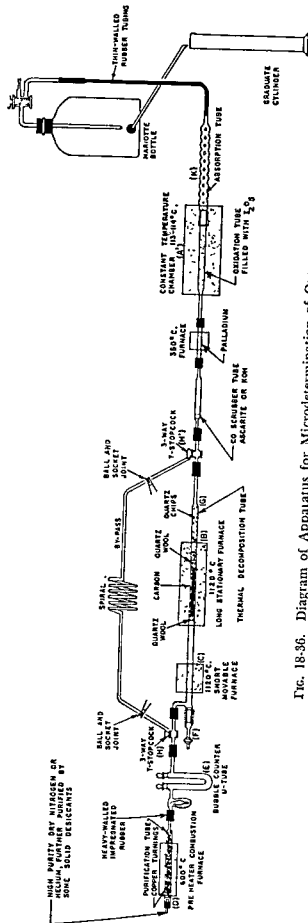


FIG. 18-36. Diagram of Apparatus for Microdetermination of Oxygen.

The excess of bromine is destroyed by introducing, drop by drop, 90% formic acid until the yellow color just disappears. The solution is allowed to stand for 5 min., after which 300 mg. of potassium iodide and 5 ml. of 10% sulfuric acid are added. The contents of the iodine flask are mixed by swirling and then titrated immediately with standardized 0.01 *N* sodium thiosulfate. The starch indicator is added when the iodine color has faded to pale yellow. Titration is continued until the disappearance of blue color.

A blank determination must be made using an identical procedure except for inserting an empty platinum boat (or capillary and platinum foil). The volume of thiosulfate solution consumed by this blank is subtracted from the volume required by the sample.

### MICRODETERMINATION OF CHLORINE, BROMINE, OR IODINE BY THE CLOSED FLASK METHOD

*Principle.*—A simple method for decomposing an organic substance to yield inorganic compounds and ions is to ignite the sample in an atmosphere of oxygen in a closed glass vessel. This method is particularly suited for micro-analysis since only a relatively small reaction vessel need be used and the danger of explosion is reduced. Thus a 10-l. bottle was employed by Hempel<sup>29</sup> for macro determinations and a 1-liter flask was recommended by Mikl and Pech<sup>30</sup> for semi-micro-analysis. Combustion operations carried out under such conditions tend to be incomplete and dangerous. On the other hand, when this technique was adapted to the micro scale by Schöniger<sup>31</sup> in 1955, it was found that the use of a 300-ml. flask always yielded satisfactory results. The simplicity of the method gained popularity for it in a very short time. This new method has been variably called the "oxygen flask method," "Schöniger method," and "closed flask combustion method." The last is favored by this writer because it is more indicative of the procedure.

Numerous publications have appeared on the discussion of the closed flask combustion method for micro-analysis. It has been utilized for the determination of halogens, sulfur, phosphorus, boron, carbon, and the metallic elements present in organic materials. A comprehensive review presented by Zarembo and Cohen<sup>32</sup> listed 122 references that cover the combustion and subsequent determinations; another review published by Macdonald<sup>33</sup> cited 62 references.

When the closed flask combustion method is utilized to determine chlorine, bromine, or iodine in an organic sample, the respective halogens are converted to the corresponding halides, which are then absorbed in a solution containing sodium hydroxide and hydrogen peroxide. The best method for the subsequent micro-determination of chloride or bromide is by means of potentiometric titration using a silver calomel or a silver-glass electrode system. Iodine is preferably determined by oxidation to iodate, followed by the liberation of iodine, which is titrated with standardized sodium thiosulfate.

*Apparatus.*—Several types of microcombustion flasks are commercially available. Figure 18-37(a) shows an example, consisting of a 300-ml. flask with a well and

<sup>29</sup> Hempel, W., *Z. Angew. Chem.*, 5, 393, 1892.

<sup>30</sup> Mikl, O., and Pech, J., *Chem. Listy*, 46, 382, 1952.

<sup>31</sup> Schöniger, W., *Mikrochim. Acta*, 1955, 123.

<sup>32</sup> Zarembo, J. E., and Cohen, L., *The Closed Flask Combustion*, multigraphed, distributed at the Metropolitan Microchemical Society, Jan. 1961, New York, N. Y.

<sup>33</sup> Macdonald, A. M. G., *Analyst*, 86, 3, 1961.

a ground-glass stopper sealed to a platinum wire basket. (Figure 18-38 shows two other types of flasks and an infrared safety igniter.)<sup>34</sup>

A simple closed flask combustion assembly may be easily constructed from a 250-ml. Erlenmeyer flask and glass stopper. A heavy (20 gauge) platinum wire is sealed to the roll of platinum foil (as shown in Fig. 18-37(b)) or rolled up to form a spiral. During combustion, the flask is placed inside an ice water bath to absorb the heat which is generated momentarily.

**Procedure. Preparation of the Sample.**—A piece of cigarette paper is cut to 18 mm. square, with a tongue 20 mm. long (as shown in Fig. 18-37(c)). For solid

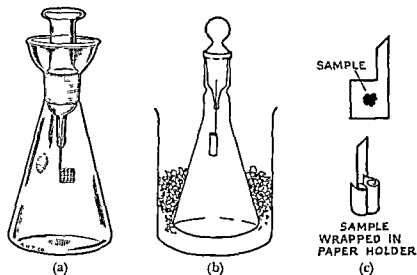


FIG. 18-37. Oxygen Combustion Flasks and Combustion Paper. (Courtesy A. H. Thomas Co.)

samples, the paper is placed on a watch glass and accurately weighed. The sample is added to the center of the paper and reweighed. Then the paper is carefully folded and inserted into the platinum basket of the combustion flask. Organic liquids are weighed in short thin-walled capillaries (Fig. 18-14). The tip of the capillary is broken off, and the capillary and tip are folded inside the paper strip, which is inserted into the platinum basket horizontally.

**Preparation of the Oxygen Flask.**—Ten ml. of distilled water, 5 ml. of 0.5 *N* sodium hydroxide, and 10 drops of 30% hydrogen peroxide are added to the combustion flask. The flask is then flushed with a rapid current of oxygen for about 3 min. to displace all the air.

**Combustion and Absorption.**—The neck of the combustion flask is wetted with distilled water. With his left hand holding the flask and his right hand holding the stopper carrying the platinum basket and paper roll, the analyst ignites the tongue of the paper over a small flame, and immediately inserts the stopper into the flask. Combustion of the organic sample takes place instantly. The stopper should be seated tightly while the flask is immersed into the ice water bath to prevent pressure build-up. After the combustion, the contents of the flask are shaken to bring all the halogens into the alkali solution.

<sup>34</sup> The flask is clamped and placed on an inclined platform. After the sample has been aligned with the beam of the infrared lamp, push button firing is done from outside the cabinet.



**Potentiometric Determination of Chloride and/or Bromide.**—The stopper of the combustion flask is lifted and the platinum basket is rinsed with water. The contents of the flask are now quantitatively transferred into a beaker. The glass-silver electrodes are inserted. Concentrated nitric acid is introduced dropwise,

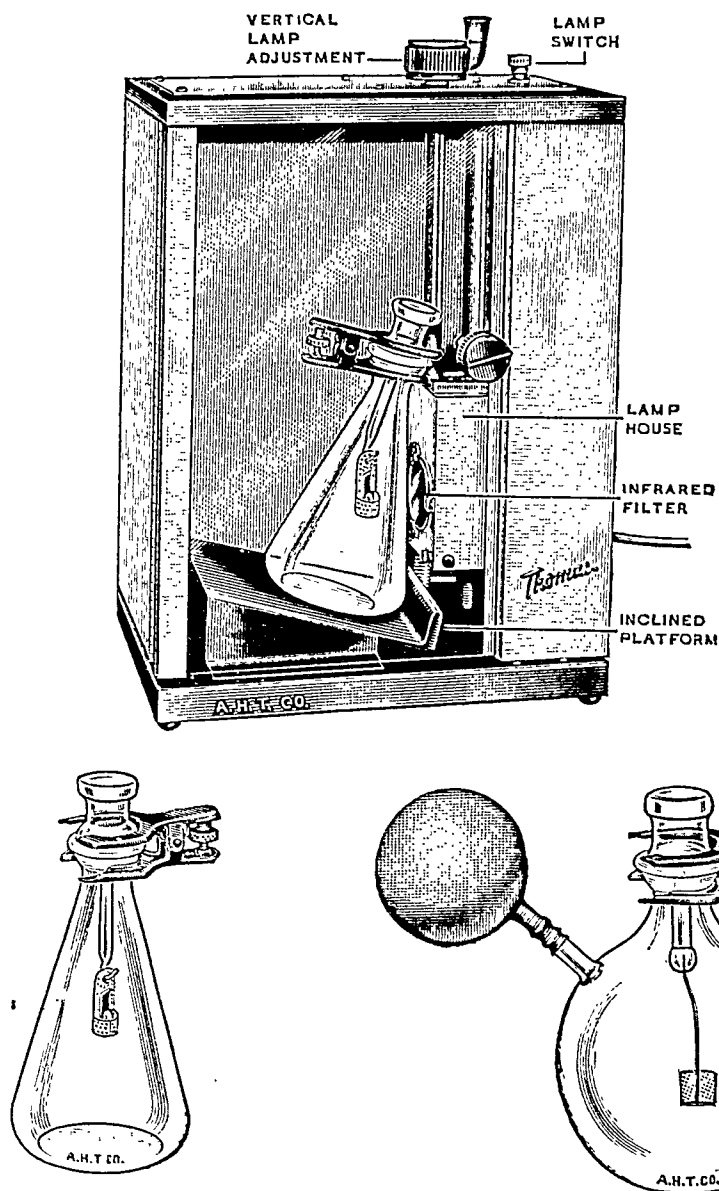


FIG. 18-38. Oxygen Combustion Flasks and IR Safety Igniter. (Courtesy A. H. Thomas Co.)

until the pH of the solution has lowered to 1. The halide solution is now titrated with standardized 0.02 *N* silver nitrate. Readings of volume and pH values are recorded and the end point is determined from the plot.

Mixtures containing bromine and chlorine give two distinct breaks. These may be used to determine each element simultaneously.

**Titrimetric Determination of Iodine.**—After removing the stopper and rinsing the platinum basket, 10 ml. of bromine-acetic acid mixture (prepared by adding 4 ml. of bromine and 100 g. of potassium acetate to 100 ml. of glacial acetic acid) are introduced into the combustion flask. Five ml. of 1 *M* sulfuric acid and a few crystals of potassium iodide are then added. The flask is again stoppered and the contents are mixed by swirling. After standing for 5 min., the iodine liberated is titrated with 0.02 *N* sodium thiosulfate solution. Starch indicator is added when the yellow color nearly disappears.

### MICRODETERMINATION OF FLUORINE BY ALKALI FUSION IN METAL BOMB

**Principle.**—Organic substances containing fluorine, especially perfluoro compounds, are resistant to the reagents and treatment ordinarily employed for quantitative organic micro-analysis;<sup>35</sup> therefore a vigorous reductive method is generally recommended. The sample is heated with metallic sodium or potassium, whereupon the organic fluorine is converted to alkali fluoride. Fluoride ions are then separated from the reaction mixture by steam distillation of fluosilicic acid in a perchloric acid solution and determined by means of thorium nitrate.

**Apparatus. Metal Bomb.**—The Parr microbomb of 2.5-ml. capacity<sup>36</sup> is suitable. The gasket should be made of copper by cutting from a sheet of copper 0.5 mm. thick.

**Distilling Apparatus.**—The distilling apparatus<sup>37</sup> is shown in Fig. 18-39. The lower section is the steam generator made from a 1-liter flat-bottomed borosilicate glass flask. It is provided with a safety tube and a side arm that serves as the outlet and is closed by a screw clamp. The upper section comprises the distilling flask and condenser. As indicated by the arrows, steam, *S*, travels along the ground-glass joint, *J*, passes through two concentric tubes, *IT* and *ET*, and reaches the distilling flask, *D*, through the two openings. The vapors enter the condenser, *C*, which consists of 3 concentric tubes. In *IT*<sub>2</sub> and *ET*<sub>2</sub>, the vapors are condensed, and in *ET*<sub>2</sub> the cooling water circulates. The ground-glass joint, *J*<sub>2</sub>, serves as the opening for the introduction of the alkali fluoride solution, as well as the seat of a thermometer during distillation, with the mercury bulb immersed in the liquid, *L*.

Since steam distillation from a perchloric acid solution requires a temperature of 135°C., an additional heating system is provided by the electric heating jacket, *H*, wound by Nichrome wire, *IV*, and covered with insulating cement.

A set of 3 distilling units may be conveniently joined together, as shown in Fig. 18-40. Each apparatus is placed on an electric hot plate, which heats the steam generator. Each heating jacket is connected to a variable resistance mounted in a wooden box covered with an asbestos-cement plate. Three metal rods are fixed at the rear of the box; rings, *R* (see Fig. 18-39 (b)) holding the heating jackets are attached to these rods.

**Equipment for Visual Titration.**—A set of 100-ml. Nessler tubes, with polyethylene caps.

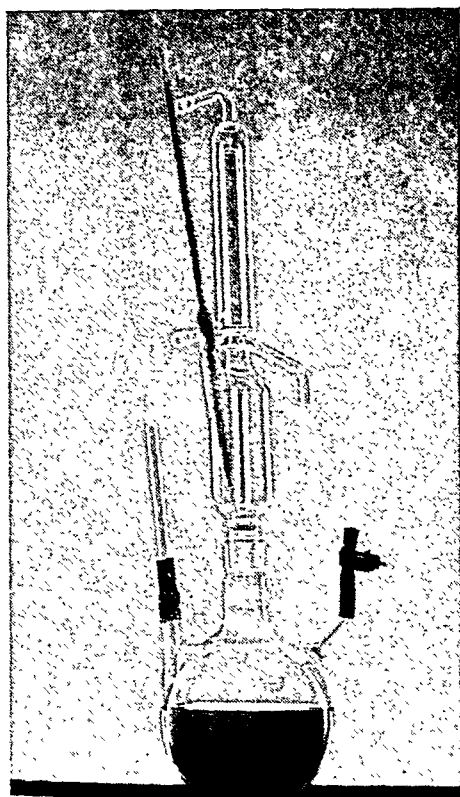
**Procedure. Preparation of the Potassium Capillary.**—In the device for the preparation of a glass capillary containing potassium (Fig. 18-41), potassium pellets are kept under kerosene in a test tube and melted on the heating stage. The glass

<sup>35</sup> Ma, T. S., *Microchem. J.*, 2, 91, 1958.

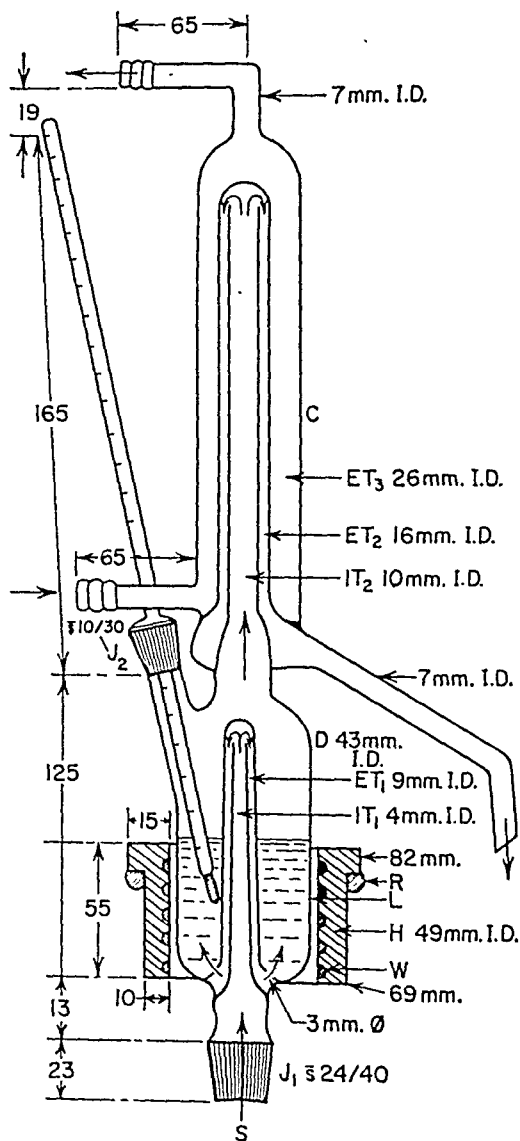
<sup>36</sup> Available from Parr Instrument Co., Moline, Ill.

<sup>37</sup> Ma, T. S., and Gwirtsman, J., *Anal. Chem.*, 29, 140, 1957.

capillary, of about 2-mm. diameter, is immersed in the molten metal, which is drawn up by the application of slight suction. The potassium in the capillary solidifies readily upon cooling. The weight of potassium metal in the capillary can be found by weighing the capillary before and after filling.



(a)



(b)

FIG. 18-39. Distilling Apparatus: (a) Complete Unit; (b) Details of Upper Part. (Upper part reprinted from *Analytical Chemistry*, 29, 141, 1957. Copyright 1957 by the American Chemical Society; reprinted by permission of the copyright owner.)

NOTE.—For samples containing low percentages of fluorine, sodium may be used in place of potassium.

**Preparation of the Sample.**—A 1- to 5-mg. sample (containing 0.1 to 0.5 mg. of fluorine) is accurately weighed out and transferred to the Parr microbomb. Solids are weighed by means of a microweighing tube (Fig. 18-12). Viscous liquids are

weighed in micro glass cups made by sealing one end of a 4-mm. glass tube. Volatile liquids are weighed in capillaries similar to that shown in Fig. 18-14 but without the air chamber. The capillary should have about a 2-mm. bore and a 15-mm. length, with a tip of the same length and 1-mm. bore. The liquid sample

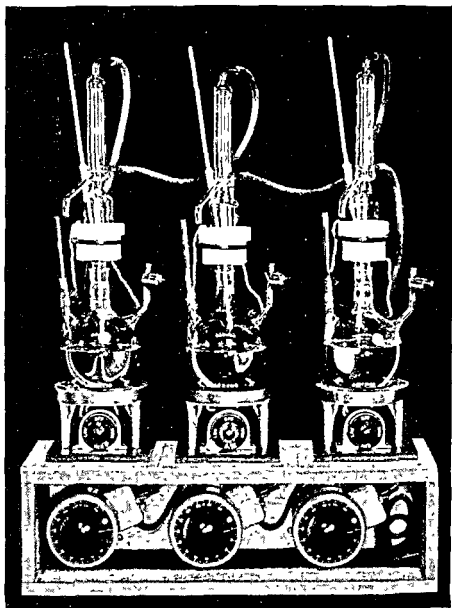


FIG. 18-40. Assembly for Microdetermination of Fluorine. (Reprinted with permission from *Microchemical Journal*, 2, 99, 1958, John Wiley and Sons, Inc.)

is introduced to the previously weighed capillary by means of a syringe, and then the capillary is sealed before the final weighing. The tip of the capillary is broken off with an ampoule cutter, and both the tip and the capillary are placed in the microbomb. The sealed capillary may be chilled in dry ice until ready for analysis.

**Alkali Fusion.**—After placing the sample inside the microbomb, a section of the potassium capillary containing about 50 mg. of the alkali metal is introduced. The microbomb is closed tightly, the copper gasket providing a resistant seal. Then

the microbomb is ignited over a Bunsen burner for 10 min. Upon cooling, the microbomb is opened and allowed to stand in the air for 5 min. The underside of the lid is now washed with fluorine-free water into a 100-ml. beaker. A trace of unreacted alkali metal in the microbomb is cautiously destroyed by adding 1 to 2 drops of water. More water is then introduced to dissolve the fusion mixture and the solution is transferred into the 100-ml. beaker. Any adhering material is removed by means of a glass rod, and the microbomb is washed thoroughly with a jet of water.

**Steam Distillation from Perchloric Acid Solution.**—The contents of the 100-ml. beaker are transferred quantitatively into the distilling apparatus, through a funnel with ground-glass joint fitted to opening  $J_2$  of Fig. 18-39. The beaker is then rinsed with 20 ml. of 70% perchloric acid, which is also transferred to the still. One milliliter of silver perchlorate solution and 10 glass beads are then added. The thermometer is placed in position and the distillation is ready to start. The hot plate switch is turned on, and the opening of the outlet tube of the steam generator is so regulated by the screw clamp that pressure corresponding to about 25 mm. of water column in the safety tube is maintained inside the flask. When the temperature of the fluoride solution (Fig. 18-39, *L*), reaches  $130^\circ\text{C}$ ., the screw clamp is closed and the steam distillation commences. At this moment the variable resistance is adjusted so that the temperature of liquid, *L*, is kept at  $135^\circ \pm 2^\circ\text{C}$ . The distillate is received in a polystyrene container, and 250 ml. of liquid are collected in about 45 min.

Then the variable resistance is turned off. When a drop in temperature is indicated in the thermometer, the outlet tube of the steam generator is opened and the hot plate is switched off.

**Determination of Fluoride.**—A suitable aliquot of the distillate (not more than 75 ml.) is adjusted in a polyethylene beaker to  $\text{pH } 3.0 \pm 0.05$ , by means of the pH meter and a few drops of dilute hydrochloric acid or sodium hydroxide solution. The solution is then transferred quantitatively into the Nessler tube. Two ml. of 0.01% sodium alizarinsulfonate indicator solution are added, and the volume is made up to 100 ml. A blank is prepared in another Nessler tube containing fluorine-free water, adjusted to the same pH, and 2 ml. of the indicator. Both solutions are of the same green color. A measured volume of the standard thorium nitrate solution (prepared by dissolving 200.00 mg. of thorium nitrate tetrahydrate in water and diluting to 1 liter) is added from a microburet to the Nessler tube containing the sample until a pronounced pink color is obtained. Exactly the same volume of standard thorium nitrate solution is added to the blank. Since the latter contains no fluoride, the color is much darker. Now the blank is back-titrated with the standard sodium fluoride solution (containing 100  $\mu\text{g}$ . of fluorine per milliliter) until the color matches the sample tube under the fluorescent lamp. The standard

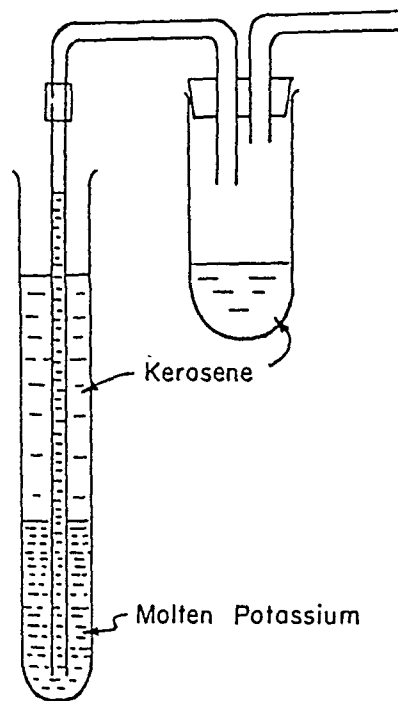


FIG. 18-41. Preparation of the Potassium Capillary. (Reprinted with permission from Microchemical Journal, 2, 97, 1958, John Wiley and Sons, Inc.)

sodium fluoride solution is added in small increments and the contents are mixed by inverting the capped Nessler tube. The amount of fluoride used for the bleaching of the lake in the blank tube corresponds to the concentration of fluoride in the unknown sample.

### MICRODETERMINATION OF SULFUR BY THE CLOSED FLASK COMBUSTION METHOD

**Principle.**—Microdetermination of sulfur by the closed flask combustion technique (see p. 389) is recommended for samples containing only carbon, hydrogen, oxygen, and sulfur. After the decomposition, sulfuric acid is obtained and determined by titration with 0.01 *N* sodium hydroxide.

**Apparatus.**—See "Microdetermination of Chlorine, Bromine, or Iodine by the Closed Flask Method," above, p. 389.

**Procedure.**—The steps for preparation of the sample, oxygen flask, combustion, and absorption are identical to those described in "Microdetermination of Chlorine, Bromine, or Iodine by the Closed Flask Method," above, p. 390, except that 5 ml. of distilled water, instead of 0.5 *M* sodium hydroxide, and 10 drops of neutralized hydrogen peroxide are used as the absorbent. After the combustion, the stopper and the platinum basket are rinsed with distilled water. The contents of the flask are gently boiled for 2 min. to remove the residual hydrogen peroxide. One drop of 0.1% methyl red indicator solution is added and the solution is titrated with standardized 0.01 *N* sodium hydroxide solution to the pink end point.

### MICRODETERMINATION OF SULFUR, CHLORINE, OR BROMINE, BY THE PREGL CATALYTIC OXIDATION METHOD

**Principle.**—In the Pregl catalytic oxidation method for the determination of sulfur or halogen, the vapor of the organic substance is mixed with oxygen and slowly conducted through sections of platinum metal heated to 900°C. in a combustion tube. The resulting sulfur or halogen compounds are retained on a glass spiral wetted with appropriate absorbent. This method may be used for the analysis of low-boiling liquids and gases that are not amenable to the closed flask combustion technique.

**Apparatus.**—The micro-combustion tube for the Pregl catalytic oxidation method (Fig. 18-42) is 730 mm. long, and has an inside diameter of 8 mm. One end contains a glass spiral formed around a central rod 230 mm. long. The spiral is held



FIG. 18-42. Microcombustion Tube for Halogen and Sulfur Determination. (Courtesy A. H. Thomas Co.)

in position in the combustion tube by an indentation in the side wall. A combustion tube in two sections (connected by ground glass joint placed near the indentation) is recommended for multiple determinations.<sup>38</sup>

The combustion furnaces used in the determination of carbon and hydrogen may

<sup>38</sup> Beazley, C. W., Ind. Eng. Chem., Anal. Ed., 11, 229, 1939.

be employed for heating the above combustion tube. It should be noted that the spiral section should protrude beyond the combustion furnace.

The platinum catalyst for the Pregl catalytic oxidation method, available from the supply house, is known as "platinum contact star" (Fig. 18-43). Rolls of platinum foil about 60 mm. long, which fit the combustion tube loosely also can serve the purpose.



FIG. 18-43. Platinum Contact Star. (Courtesy A. H. Thomas Co.)

**Procedure. Assembling the Apparatus.**—Into a large test tube of 30-mm. diameter and 130-mm. length is added a convenient volume of the appropriate absorbent liquid for the determination of sulfur (about 10 ml. of 6% hydrogen peroxide solution) and halogens (10 ml. of 20% sodium carbonate mixed with 0.5 ml. of saturated hydrazine sulfate solution) respectively. The constricted end of the microcombustion tube is immersed in the absorbent liquid while the open end is protected with a cotton-filled air filter. Gentle suction is applied by mouth to draw up the absorbent liquid until the entire glass spiral is covered. It is important to watch that no air is sucked into the combustion tube and that the liquid does not go beyond the glass spiral. Then the combustion tube is lifted up to drain the absorbent liquid along the walls of the large test tube. The latter is emptied but need not be rinsed.

The combustion tube is now placed on the combustion stand in such a way that the glass spiral protrudes outside the combustion furnace. The large test tube is inserted to cover the tip of the combustion tube and part of the glass spiral. The cotton-filled air filter is removed and 2 platinum contact stars are pushed consecutively into the combustion tube until they are inside the long furnace. The open end of the combustion tube is connected, by means of a rubber stopper carrying a fine-tapered glass tubing, through a bubble counter to a cylinder of oxygen.

**Combustion of the Sample.**—The sample is weighed in a microboat or capillary as described in the determination of carbon and hydrogen (p. 372). The long furnace is switched on to maintain a temperature of 900°C., while oxygen passes through at the rate of 1 to 2 bubbles per sec. The rubber stopper is now removed to introduce the sample, which is pushed forward until it stands within 60 mm. of the long furnace. The rubber stopper is replaced and the combustion is started by placing the Bunsen burner (or short electric furnace) to the right of the sample and gradually advancing the burner towards the long furnace. The organic sample is slowly vaporized, and then enters the hot platinum contact stars where it is catalytically oxidized. The products formed are driven towards the wetted glass spiral. When sulfur is present in the sample, it usually occurs that a liquid drop, sulfuric acid, collects between the indentation of the combustion tube and the long furnace. When the combustion is finished, both the long furnace and the Bunsen burner are turned off.

**Gravimetric Determination of Sulfate.**—Gravimetric determination of organic sulfur is recommended when the sample contains halogen, nitrogen, or phosphorus. After the catalytic oxidation and absorption, the sample container and platinum contact stars are withdrawn from the microcombustion tube. With the large test tube supporting the tip of the combustion tube, the latter is clamped vertically, and distilled water is rapidly run into the combustion tube through the open end until the glass spiral is entirely covered. The washing is collected in the large test tube, and the combustion tube is rinsed again.

The contents of the test tube are quantitatively transferred to a black glazed crucible that has been previously weighed with the accompanying filter stick, the latter being now joined to the rubber connection of the siphon in the filtration apparatus, as shown in Fig. 18-44. One ml. of 10% barium chloride solution is added. The reaction mixture is evaporated at 100°C. on the metal block (or water

bath) to nearly dryness in order to coagulate the precipitate. Upon cooling, 5 ml. of water containing one drop of dilute hydrochloric acid are added, and the solution is filtered through the filter stick. The residue in the crucible is rinsed twice with distilled water. The crucible together with the accompanying filter stick is then dried at 125°C. on the metal block<sup>39</sup> and reweighed. The increase in weight gives the amount of barium sulfate.

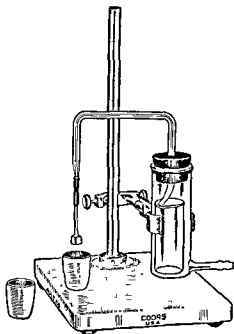


FIG. 18-44. Filtration by Porcelain Filter Stick (Reprinted with permission from Steyermark, A. Quantitative Organic Microanalysis, 2nd Ed., Academic Press, New York, 1961.)

**Gravimetric Determination of Chloride or Bromide.**—Occasional analysis of chlorine or bromine in organic compounds can be carried out advantageously by using the gravimetric method, since it does not require a standardized silver nitrate solution and the potentiometric microtitration assembly. After washing and rinsing the glass spiral of the combustion tube, as described in the preceding paragraphs, the halide solution is retained in the large test tube. Three drops of 30% hydrogen peroxide are added and the test tube is placed in a boiling water bath for 5 min. The test tube is then placed in a beaker containing cold water. Two ml. of concentrated

nitric acid are added, followed by 2 ml. of 5% silver nitrate solution. Precipitation of silver halide presents a cloudy appearance. A small beaker is inverted over the test tube, the water bath is now heated to boiling. Then the test tube and its contents are allowed to cool in the water bath in the dark until the silver halide coagulates and settles at the bottom, leaving a clear supernatant liquid. Meanwhile a filter tube is prepared, weighed and connected to the filtration assembly, as shown in Fig. 18-45. Then the siphon tube is immersed in the clear liquid in the large test tube until the lower end is about 10 mm. above the precipitate at the bottom of the test tube. A layer of 95% ethanol is carefully introduced into the large test tube without disturbing the silver halide. A slight suction is applied to draw the liquid through the filter tube. After the aqueous solution has been replaced by ethanol, and with the precipitate always covered by some liquid, the large test tube is raised in such a way that the silver halide precipitate is conducted into the siphon tube and transferred onto the filter paper above the sintered glass. The large test tube and siphon are rinsed with distilled water and 95% ethanol successively. Then the siphon tube is removed. The filter tube and its contents are dried at 105°C. for 10 min. on the drying device,<sup>40</sup> cooled to room temperature and reweighed.

<sup>39</sup> Ma, T. S., Kaïmowitz, K., and Benedetti-Pichler, A. A., *Mikrochim. Acta*, 1954, 651.

<sup>40</sup> Maurmeyer, R. K., and Ma, T. S., *Mikrochim. Acta*, 1957, 563.



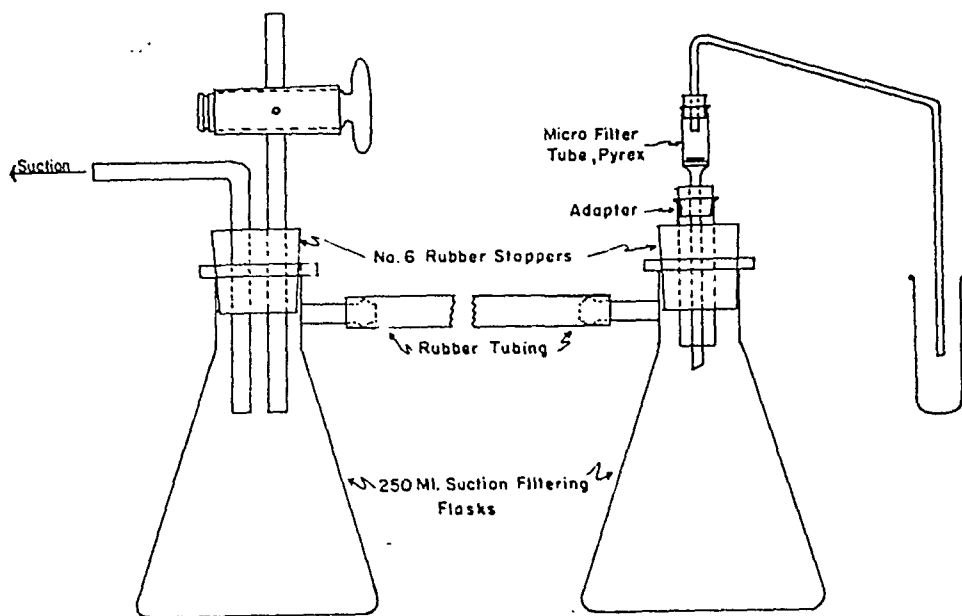


FIG. 18-45. Filtration by Means of the Filter Tube.

## MICRODETERMINATION OF PHOSPHORUS

**Principle.**—When an organic compound containing phosphorus is oxidized, the phosphorus is converted to phosphorus pentoxide, which dissolves in water to yield phosphate ions. For samples containing microgram amounts of phosphorus, the resulting phosphate is best determined colorimetrically in the form of the blue phosphomolybdate complex.<sup>41</sup> This colored complex, however, is not stable and hence, carefully controlled conditions are required. On the other hand, the yellow-colored phosphovanadophosphate complex is stable and obeys the Beer's law over a wide range of phosphorus concentration in the solution. Therefore, the latter is recommended for the microdetermination of phosphorus.<sup>42</sup>

**Apparatus.** Micro-Kjeldahl Digestion Flask.—See "Microdetermination of Nitrogen by the Kjeldahl Principle," p. 383.

**Spectrophotometer.**—Any type.

**Procedure.** Oxidation in Open Flask.—From 3 to 10 mg. of the organic substance, corresponding to 0.2 to 1.5 mg. of phosphorus, are weighed in a long-handled weighing tube (Fig. 18-12) or porcelain microboat, and transferred into the bottom of a 10-ml. micro-Kjeldahl digestion flask. After introducing 1.5 ml. of concentrated sulfuric acid, 4 drops (0.2 ml.) of concentrated nitric acid are added. The flask is heated gently on the digestion rack until the reaction subsides. The contents of the flask are cooled slightly, 2 more drops of concentrated nitric acid are added, and the flask is again heated with a medium flame until the solution becomes clear, and sulfur trioxide fumes are evolved. The reaction mixture is cooled; water is added to make up the volume to about 10 ml. The contents of the digestion flask are then quantitatively transferred, with several rinsings, to a 100-ml. volumetric flask.

<sup>41</sup> Horecker, B. L., Ma, T. S., and Haas, E., J. Biol. Chem., 136, 775, 1940.

<sup>42</sup> Ma, T. S., and McKinley, J. D., Jr., Mikrochim. Acta, 1953, 4.

**Oxidation in Closed Flask.**—The procedure described under the "Kjeldahl Principle," p. 384, is followed, using 10 ml. of distilled water as the absorbing liquid. One ml. of dilute sulfuric acid may be added to the absorbent; however, the use of sodium hydroxide-bromine mixture as absorbent<sup>43</sup> appears to have adverse effects. Cohen and Czech<sup>44</sup> have found that absorption of phosphorus pentoxide is slow in sodium hydroxide solution; Gedansky and co-workers<sup>45</sup> have pointed out that the presence of bromine interferes with a colorimetric finish and must be destroyed. After the closed flask combustion, the contents of the flask are boiled for 10 min. in order to convert all the phosphate to the ortho-form. The solution is then quantitatively transferred into a 100-ml. volumetric flask.

**Colorimetric Determination of Phosphate.**—A standard curve for the yellow phosphovanadomolybdate complex is prepared as follows. Ten aliquot portions of the standard phosphate solution (prepared from pure potassium dihydrogen phosphate and containing 0.500 mg. of phosphorus per milliliter) are accurately measured from a microburet into separate 100-ml. volumetric flasks to cover the range from 0.10 to 2.00 mg. phosphorus. A blank is also prepared. The aliquots are diluted to 65 ml. and are treated with 1.4 ml. of concentrated sulfuric acid. Then 10 ml. of ammonium vanadate solution (prepared by dissolving 2.35 g. of ammonium metavanadate and 100 ml. of 1:12 sulfuric acid in 500 ml. of boiling distilled water and diluting to 1 liter after cooling) is added slowly, with continuous swirling, into each flask. This is followed by 10 ml. of ammonium molybdate solution (prepared by dissolving 122 g. of ammonium molybdate tetrahydrate in 880 ml. of distilled water). Then the flask is filled to the 100-ml. mark with distilled water. After standing for 30 min., the yellow color is compared with the blank, which contains all the reagents and no phosphorus, and the absorbance at 410  $m\mu$  is measured. A straight line is obtained by plotting absorbance ( $A = -\log T$ ) against milligrams of the phosphorus in the solution, and from the slope and intercept of this line, an equation can be derived of the form

$$W = \alpha A + \beta$$

that gives the weight,  $W$ , of phosphorus in terms of absorbance,  $A$ .

The solution containing the phosphate produced from the sample is treated exactly as the standard phosphorus solution, and its absorbance is measured at 410  $m\mu$ . The amount of phosphorus in the sample is obtained either from the standard curve or the above equation. Since the yellow phosphovanadomolybdate complex is stable for many days it is advisable to develop the color solutions of several samples and measure their respective absorbance when convenient. It has been found that, when new reagents are prepared, only the intercept  $\beta$  of the equation is changed. Therefore, it is not necessary to plot new standard curves from time to time. The new value of  $\beta$  may be obtained by analyzing a pure known phosphorus compound simultaneously with the unknown sample.

### MICRODETERMINATION OF ARSENIC

**Principle.**—Organically bound arsenic is oxidized to arsenic acid by heating with nitric acid in dilute sulfuric acid solution. The resulting pentavalent arsenic is then determined iodometrically.

<sup>43</sup> Belcher, R., and Macdonald, M., *Talanta*, **1**, 185, 1958.

<sup>44</sup> Cohen, L. E., and Czech, F. W., *Chemist-Analyst*, **47**, 86, 1958.

<sup>45</sup> Gedansky, S. J., Bowen, J. E., and Milner, O. I., *Anal. Chem.*, **32**, 1447, 1960.

**Apparatus.** Micro-Kjeldahl Digestion Flask.—See “Microdetermination of Nitrogen by the Kjeldahl Principle,” p. 384.

**Procedure.**—The sample is accurately weighed in a long-handled weighing tube or a microboat, and transferred to the bottom of the micro-Kjeldahl digestion flask. One ml. of 30% sulfuric acid is added to cover the sample, and the digestion flask is gently heated on the stand. A few drops of concentrated nitric acid are added to facilitate oxidation. If the contents of the digestion flask do not clarify in 10 min., indicating incomplete destruction of the organic matter, the digestion flask is removed from the stand. After cooling slightly, a few drops of 30% hydrogen peroxide are added (*Caution!*) and the reaction mixture is again gently boiled. This operation may be repeated until the solution becomes colorless. Then the contents of the digestion flask are evaporated until sulfur trioxide fumes are evolved. Upon cooling, 1 ml. of distilled water is added and the contents of the flask are quantitatively transferred to a 125-ml. iodine flask. Twelve ml. of concentrated hydrochloric acid are added, followed by 1 ml. of freshly prepared 10% potassium iodide solution. The iodine flask is stoppered and its contents thoroughly mixed. After standing for 3 min., the iodine that is liberated is titrated with standardized 0.01 *N* sodium thiosulfate. The starch indicator is added when the color of the solution becomes very faint, and titration is continued until the blue color disappears. A blank should be run for the reagents used and subtracted.

## MICRODETERMINATION OF METALLIC ELEMENTS IN ORGANIC COMPOUNDS

**Principle.**—With a few exceptions (e.g., organo mercury, arsenic, and osmium compounds) an organic sample containing metallic elements leaves a residue in the microboat when it is analyzed for carbon and hydrogen, or for halogens and sulfur by the Pregl catalytic oxidation procedure. It is always advisable to weigh and investigate such residue after the combustion. Besides providing information as to the retention of carbon, sulfur, or halogens in the sample container (thus leading to erroneous results), the metallic element often may be determined directly in the microboat without utilizing a new sample.

Metals that can be determined as residue (known as ash) after the destruction of the organic material are divided into 3 categories: (a) metals that are stable in the free state, e.g., platinum, gold, and silver; (b) metals that form stable oxides but not sulfates, e.g., copper, iron, and silicon; and (c) metals that form stable sulfates, e.g., sodium, potassium, calcium, and barium. The reagent employed for the determination depends on the ash desired, as described in the procedure below.

**Apparatus.** For Ashing in Microboat.—A microcombustion tube (Fig. 18-46) may be used.

**For Ashing in Microcrucible.**—A 1.5-ml. capacity platinum microcrucible, fitted with platinum lid is desirable, although porcelain ware also may serve the purpose.

**Procedure.** When Microboat is Employed.—The organic substance is accurately weighed in a platinum microboat. If the sample is obtained after combustion (such as in carbon and hydrogen analysis), and there has been no spattering of the contents of the microboat, the latter is removed from the microcombustion train and reweighed. In either case, the microboat containing the sample is placed on the metal block of the microdesiccator (Fig. 18-17). About 20  $\mu$ l. (half a drop) of

the oxidizing agent are introduced by means of a fine capillary. Dilute nitric acid (1:1) is used for determination of the metallic element as free metal or oxide; 20% sulfuric acid is employed for determination as sulfate. The acid should be added along the walls of the microboat and should just wet the sample. The microboat is

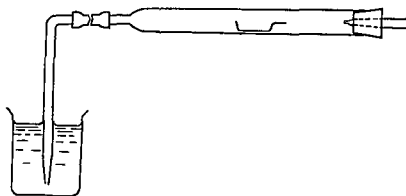


FIG. 18-46. Determination of Metal in Microboat.

then placed inside the microcombustion tube as shown in Fig. 18-48. The wide end of the combustion tube is connected to a demonstration bottle of oxygen, while the constricted end is joined, through a rubber tubing, to a bent tube with a capillary tip immersed in water. A slow current of oxygen is passed through the combustion tube while the microboat is gradually heated to prevent spattering of the sample. After the acid fumes have been driven off, the microboat is heated at high temperature. Upon cooling, the microboat is withdrawn and weighed with the ash. This process of adding acid, heating, and weighing is repeated until there is no change in weight of the contents of the microboat. The percentage of metal present in the original sample is then calculated from the weight of the ash and its chemical composition.



FIG 18-47. Determination of Metal in a Microcrucible.

Some metals, such as nickel, do not form stable sulfates, and give oxides of indefinite composition. A convenient way to determine such a metallic element is through the combination of oxidation with a subsequent reduction process. After the mixed oxides are obtained as described in the last paragraph, the bottle of oxygen is exchanged with hydrogen. Hydrogen is passed through the combustion tube for a few minutes

to displace all oxygen in the tube. Then a small flame is placed under the microboat, and the oxides are converted to the free metal. Precautions should be taken to prevent the exhaust hydrogen from catching fire.

**When Microcrucible is Employed.**—The platinum microcrucible is the equipment of choice for the determination of metals in organic materials because it is much deeper than the microboat and has a wider bottom. The sample is weighed into the bottom of the microcrucible, which has been previously weighed with its lid. The crucible is then seated on a large platinum crucible cover supported on a silica triangle. A microdrop of the oxidizing acid is added along the walls and the microcrucible lid is replaced. A very small flame is applied to the side of the

microcrucible (see Fig. 18-47). When no more acid fumes escape through the lid, the burner is shifted to a position under the large platinum crucible cover to heat the bottom of the microcrucible with a strong flame for two min. The crucible, lid, and ash are weighed upon cooling. This process is then repeated. If duplicate analysis is desired, another sample may be weighed into the microcrucible without removing the ash.

### MICRODETERMINATION OF MERCURY

**Principle.**—The microdetermination of mercury is based on its volatility. The organic material is decomposed by heat in a combustion tube and the vapors are conducted through a section of calcium oxide, maintained at  $700^{\circ}\text{C}$ . The mercury vapor is then driven into a small tube packed with gold, retained as amalgam, and weighed.

**Apparatus.**—The combustion assembly is shown in Fig. 18-48. The microcombustion

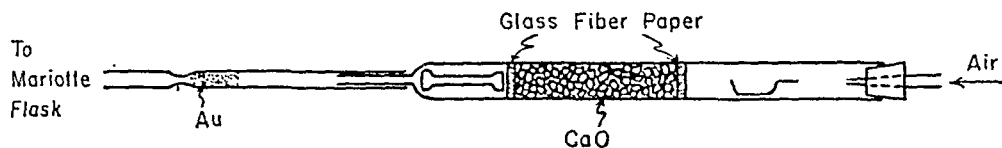


FIG. 18-48. Assembly for Microdetermination of Mercury.

tion tube is packed with a column of granular calcium oxide about 120 mm. long, held between 2 pieces of glass fiber paper.<sup>46</sup> A 50-mm. long glass rod with flattened ends provides an empty space between the combustion furnace, which heats the section of calcium oxide only, and the constricted end of the combustion tube. The wide end of the combustion tube is connected to the air holder through a bubble counter—U-tube (Fig. 18-21 D).

The absorption tube for mercury is 80 mm. long and 8 mm. in diameter. It is drawn out to a tip 3 mm. in diameter and 20 mm. long. A 40-mm. layer of shredded gold leaf is packed at the end. The tip of the absorption tube is connected to the Mariotte bottle (Fig. 18-21 K).

**Procedure.**—The sample (5 to 10 mg.) is weighed in a porcelain or silica microboat and introduced into the combustion tube to within 50 mm. of the calcium oxide. With the section of calcium oxide maintained at  $700^{\circ}\text{C}$ ., a slow current of dry air is passed through the combustion tube while the leveling tube of the Mariotte bottle is lowered to produce a suction effect on the absorption tube. In this way the vapors coming out of the combustion tube will be drawn through the gold-packed absorption tube, which was previously weighed.

The Bunsen burner is now gradually moved forward until the vapors have distilled into the calcium oxide layer, where all sulfur and halogens are retained, and the mercury passes into the cool, empty part of the combustion tube.

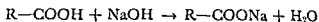
With a piece of clean, wet cloth placed over the absorption tube, a small flame is carefully applied to the constricted end of the combustion tube so that all mercury is driven into the absorption tube and converted into gold amalgam. After aspirating 50 ml. more of air through the absorption tube, it is detached, wiped externally, placed inside a desiccator containing silica gel with indicator for 30 min., and reweighed.

<sup>46</sup> Ma, T. S., and Benedetti-Pichler, A. A., *Anal. Chem.*, **25**, 999, 1953.

## MICRODETERMINATION OF ORGANIC FUNCTIONAL GROUPS

MICRODETERMINATION OF THE CARBOXYL GROUP  
BY AQUEOUS ACIDIMETRY

*Principle.*—The carboxyl group may be determined by titration with 0.01 *N* aqueous sodium hydroxide in the absence of carbon dioxide.



Alcohol is used as solvent for the sample, and also to suppress the hydrolysis of the sodium carboxylate.

*Apparatus. Microburets.*—The Pregl microburet with automatic zero arrangement (Fig. 18-49) has a capacity of 10 ml., and is graduated in 0.05 ml. (Microburets with 10-ml. capacities and 0.02-ml. graduations are available from European supply houses.) The reservoir has 1-liter capacity. A set of 2 microburets can be conveniently placed on one stand. One microburet is for standard solution of 0.01 *N* hydrochloric or sulfuric acid or potassium biniodate; the other is for 0.01 *N* sodium hydroxide. The stopcock for delivery of sodium hydroxide should be made of Teflon; if this is not available, the stopcock should be replaced by a rubber connection carrying a glass bead or a pinch clamp (as shown in the figure).

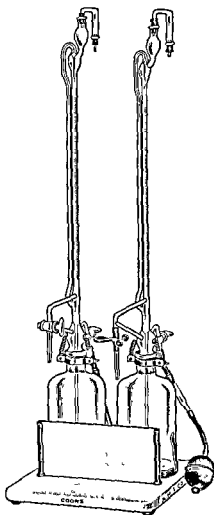
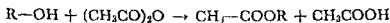


FIG. 18-49. Pregl Microburets  
(Courtesy A. H. Thomas Co.)

*Procedure.*—The sample, containing 0.05 to 0.1 milli-equivalent of carboxyl group, is accurately weighed, by means of the weighing tube (Fig. 18-12) or a microboat, into a 50-ml. Erlenmeyer flask. Five ml. of 50% ethanol, which was previously neutralized, are added, followed by two drops (0.06 ml.) of 1% phenolphthalein indicator solution. The solution is brought to boiling over a small flame, and then titrated while warm with the standardized 0.01 *N* sodium hydroxide. The contents of the flask are boiled again near the end point, and the titration is completed when a faint pink color persists for 30 sec. In case the solution has been over-titrated, 1.00 ml. of the standardized 0.01 *N* hydrochloric acid is introduced and then back-titrated with the 0.01 *N* sodium hydroxide to the faint pink end point.

MICRODETERMINATION OF THE HYDROXYL GROUP  
BY ACETYLATION

*Principle.*—The hydroxyl group is usually determined by acetylation with a known excess amount of acetic anhydride in a sealed tube.



Pyridine, used as the solvent, also serves to drive the reaction to completion by combining with the liberated acetic acid. After the esterification, the excess of acetic anhydride is hydrolyzed by adding water to the reaction mixture. The total amount of acetic acid in the resulting solution is then determined by titration with standardized sodium hydroxide solution.

**Apparatus. Reaction Tubes.**—The reaction tubes are prepared as follows: a piece of 6-mm. soft glass tubing, about 140 mm. long, is heated at the center until the glass softens; it is then pulled apart rapidly; the drawn out section is cut off at a point where the tubing has narrowed to about 2 mm. in diameter; this end is closed in the flame to form a round bottom; 2 reaction tubes, each about 60 mm. long, are constructed from a length of glass tubing. One tube is used to hold the sample, while the other tube serves as the blank.

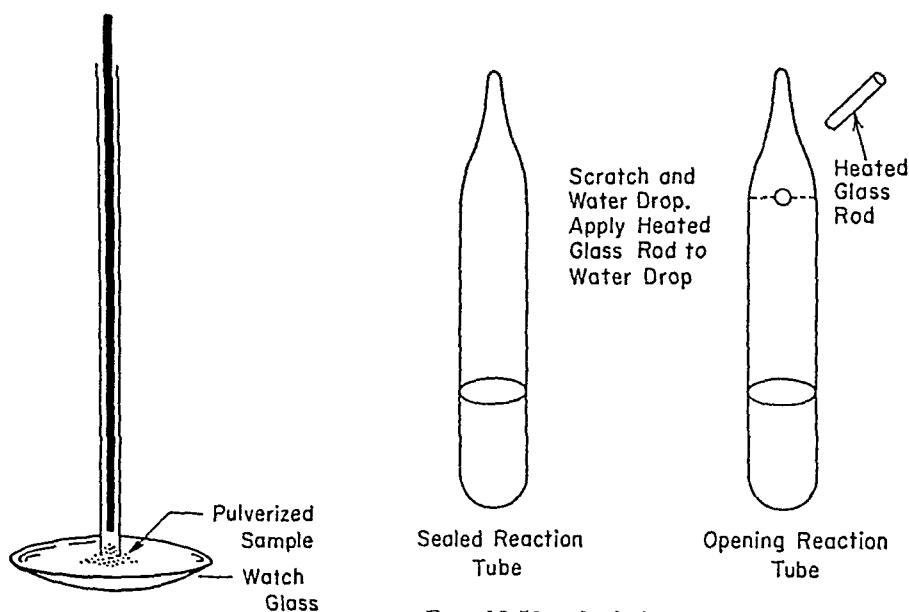


FIG. 18-50. The Capillary-and-Plunger Technique for Introducing Solid Sample.

FIG. 18-51. Sealed Reaction Tube for Micro Acetylation.

**Procedure. Preparation of the Sample.**—The reaction tube is placed in a stand or small beaker and weighed to  $\pm 0.01$  mg. If the sample to be analyzed is a solid, it is introduced by the capillary-and-plunger technique as shown in Fig. 18-50. The capillary is pushed into the pulverized sample so that an amount containing about 0.1 milli-equivalent of hydroxyl group is trapped inside. The outside walls of capillary are wiped with a small brush. Then the capillary, with the sample, is carefully lowered into the previously weighed reaction tube until the tip of the capillary is about 5 mm. from the bottom of the reaction tube. The sample is pushed out by means of the plunger and the capillary, together with the plunger, is carefully withdrawn. The increase in weight of the reaction tube is recorded.

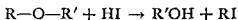
If the sample is a liquid, it is delivered into the previously weighed reaction tube by means of a syringe with a long needle. Care should be taken so that no liquid touches the upper walls of the reaction tube.

**Acetylation.**—After the sample has been weighed into the reaction tube, a volume of the acetylating agent (prepared by mixing 10 ml. of reagent grade acetic anhydride with 30 ml. of reagent grade pyridine), estimated to be about 200 mole-per cent in excess, is introduced by means of a long capillary pipet. The increase in weight of the reaction tube is again noted. The reaction tube is then sealed to form a tapered tip about 20 mm. long (Fig. 18-51). A blank containing the same amount of acetylating agent is prepared in the second reaction tube, which is weighed and sealed. The 2 sealed tubes are inverted several times to mix the contents. They are now heated in a boiling water bath for 1 hr. and then cooled to room temperature.

**Titration.**—The sealed reaction tube is opened in the following manner: with a glass cutter, a line is scratched on the tube about 20 mm. from the tip; the tube is cracked by touching a hot glass bead on the scratch; the tip is dropped into a 50 ml. Erlenmeyer flask containing 5 ml. of distilled water; the contents of the reaction tube are emptied into the same Erlenmeyer flask, and the tube is rinsed with 1 ml. of distilled water; another scratch is made near the closed end of the reaction tube, which is again cracked with a hot glass bead; the remaining parts of the reaction tube are all dropped into the Erlenmeyer flask; the Erlenmeyer flask is then swirled to effect complete hydrolysis of the residual acetic anhydride; 2 drops (0.08 ml.) of 1:3 cresol red-thymol blue mixed indicator solution are added, and the contents of the flask are titrated with standardized 0.05 *N* ethanolic sodium hydroxide. The end point is indicated by a color change from yellow to blue.

### MICRODETERMINATION OF THE ALKOXYL GROUP BY HYDROGEN IODIDE CLEAVAGE

**Principle.**—The alkoxy group is separated from the rest of the organic molecules on heating the sample with hydriodic acid, giving rise to a hydroxy compound and an alkyl iodide.



The alkyl iodide is separated from the reaction mixture by virtue of its volatility. The vapor is then absorbed in acetic acid containing bromine, which oxidizes the iodide to iodic acid. The determination is finished titrimetrically through the liberation of iodine, and titration of the liberated iodine with 0.05 *N* sodium thiosulfate.

**Apparatus.** *Micro Alkoxy Apparatus.*—The apparatus<sup>47</sup> recommended by the Committee on Microchemical Apparatus, Division of Analytical Chemistry, American Chemical Society (Fig. 18-52), is composed of 4 parts: (a) the round reaction flask; (b) the condenser with scrubber; (c) the delivery tube; and (d) the receiving tube. This apparatus is suitable for the determination of methoxyl and ethoxyl groups but not for higher homologs.

**Procedure.** *Preparation of the Apparatus.*—The receiving tube is filled with 5 ml. of acetic acid containing 10% sodium acetate. Six drops of bromine are added and the apparatus is assembled (as shown in Fig. 18-52). The scrubber is filled with equal volumes of 5% cadmium sulfate and 5% sodium thiosulfate solutions.

**Preparation of the Sample.**—The sample is accurately weighed, by means of the weighing tube or microboat, into the reaction flask. A small crystal of phenol and 0.2 ml. of propionic anhydride are added as solvent. With the side arm of the

<sup>47</sup> Steyermark, A., et al., *Anal. Chem.*, **28**, 112, 1956.



reaction flask connected through a rubber tubing to a demonstration bottle of nitrogen, 8 ml. of hydriodic acid (sp. gr. 1.7) are added, and the flask is quickly attached to the condenser.

**Decomposition and Absorption of Alkyl Iodide.**—While a current of nitrogen is passed through the apparatus at the rate of about one bubble per sec., the solution in the reaction flask is gently boiled for 30 to 60 min. Then the receiving tube is

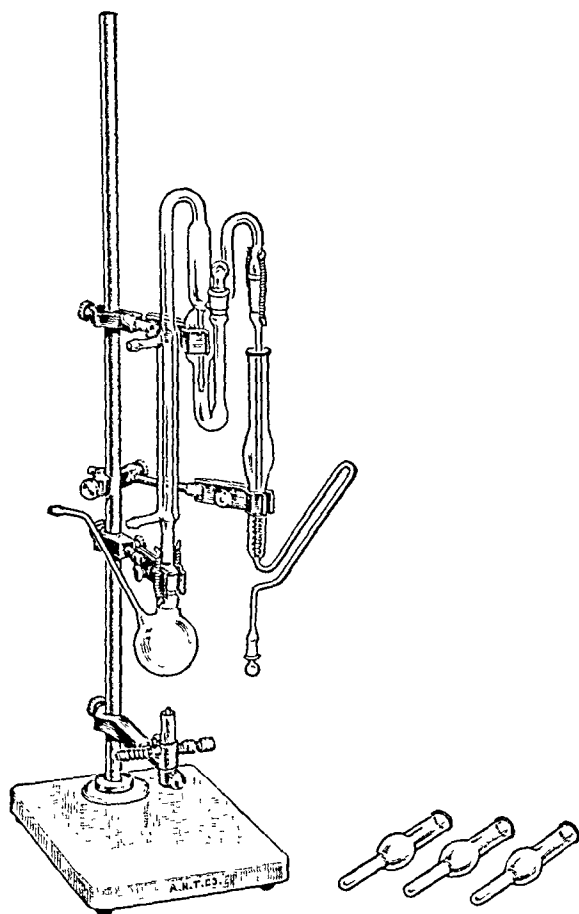


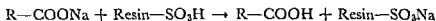
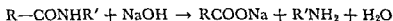
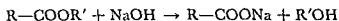
FIG. 18-52. Micro Methoxyl-Ethoxyl Apparatus. (Courtesy A. H. Thomas Co.)

lowered. The delivery tube is disconnected and rinsed with a little distilled water.

**Titration.**—A 125-ml. iodine flask containing 5 ml. of 10% sodium acetate in acetic acid is placed under the receiving tube. The stopper at the bottom of the receiving tube is carefully detached to allow the contents of the receiving tube to run into the iodine flask. The receiving tube is thoroughly rinsed with distilled water and the rinsings are collected in the iodine flask. The flask is swirled to mix the contents. Formic acid is now added dropwise until the bromine color just vanishes. The iodine flask is stoppered and shaken occasionally during the addition of formic acid. Then 2 ml. of 10% potassium iodide solution are introduced, followed by 3 ml. of 10% sulfuric acid. The iodine flask is stoppered, shaken, and allowed to stand for 5 min. The liberated iodine is now titrated with the standardized 0.05 *N* sodium thiosulfate to the starch end point.

### MICRODETERMINATION OF THE ACYL GROUP BY ION EXCHANGE

**Principle.**—The acyl group in esters and amides is liberated by hydrolysis in alcoholic sodium hydroxide solution followed by exchange with a strongly acidic resin.



The free carboxylic acid in the eluate is then determined by titration with standard 0.02 *N* sodium hydroxide solution.

**Apparatus.** *Ion-exchange Column.*—The ordinary 10-ml. buret, which has 0.1-ml. graduations, and has a length of 150 mm. and bore of 10 mm., is suitable as the ion-exchange column.

**Procedure.** *Preparation of the Ion-exchange Column.*—The bottom of the ion-exchange column is packed with a 3-mm. layer of glass wool, and the buret is clamped on a stand. A suspension of 1 g. of Amberlite IR-120 (or other sulfonic acid type resin) in 20 ml. of dilute hydrochloric acid is transferred into the column to give a resin bed about 80 mm. long. The resin is covered with another layer of glass wool and then washed with distilled water until the eluate is free from hydrochloric acid as shown by the silver nitrate test. The resin beads should be covered with liquid all the time, and the ion-exchange column should be stoppered when not in use.

**Preparation of the Sample and its Hydrolysis.**—A sample containing about 0.1 milli-equivalent of the acyl group is accurately weighed and transferred into the bottom of a 10 by 75 mm. test tube (preferably without flange). One ml. of *n*-amyl alcohol is added, followed by 0.10 ml. of the alkali reagent (prepared by dissolving 3.6 g. of reagent grade sodium hydroxide in 30 ml. of *n*-amyl alcohol). The test tube is then sealed to form a tapered tip (see Fig. 18-51).

The sealed tube is placed in a metal block and heated at 150°C. for 1 hr. After cooling, the tip of the tube is opened by a sharp flame to release the gas pressure. A scratch is made on the upper part of the tube, a drop of water is placed on the scratch, and the top of the tube is broken off by applying a hot glass bead on the scratch.

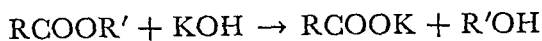
**Liberation and Titration of the Free Carboxylic Acid.**—To the test tube containing the above reaction mixture are added 3 ml. of a solvent containing 4 parts of isopropyl alcohol and 6 parts of water. The contents of the test tube are mixed by swirling and then transferred quantitatively into the ion-exchange column, the stopcock of the column being closed. The test tube is rinsed 3 times with 2-ml. portions of the same solvent, and the rinsings are transferred into the ion-exchange column. Then a 125-ml. Erlenmeyer flask is placed under the ion-exchange column and the stopcock is opened so that the eluate runs into the flask at the rate of 1 to 2 ml. per min. Five ml. of the water-isopropyl alcohol mixed solvent are added into the ion-exchange column when the liquid level inside the column approaches the glass wool above the resin beads. This process is repeated 3 times before the stopcock is closed. About 25 ml. of eluate will have been collected.

The free carboxylic acid solution collected in the Erlenmeyer flask is titrated as follows: if the eluate is colorless, 4 drops of 1% phenolphthalein indicator are added, and the solution is titrated with the standardized 0.02 *N* sodium hydroxide

until a faint pink color appears and persists for 30 sec. If the eluate is slightly yellow, 4 drops of a mixed indicator containing 1 part of 0.1% aqueous cresol red and 3 parts of 0.1% aqueous thymol blue are added, and the solution is titrated with the standard alkali until its yellow color turns bluish violet.

### MICRODETERMINATION OF THE SAPONIFICATION NUMBER OF AN ESTER

**Principle.**—The ester is saponified by heating with a known amount of potassium hydroxide in an organic solvent in a sealed tube.



The residual alkali is then determined by titration with standardized hydrochloric acid solution. The saponification number is the weight in milligrams of potassium hydroxide that would have been consumed by 1.00 g. of the sample.

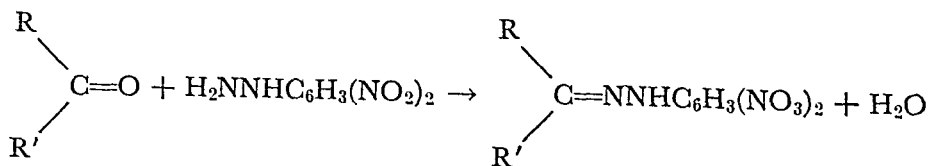
**Apparatus. Reaction Tube.**—The reaction tube is prepared from 8-mm. borosilicate glass tubing in the manner described previously in "Microdetermination of the Hydroxyl Group by Acetylation," p. 405.

**Procedure.**—The reaction tube is placed on a stand and weighed to  $\pm 0.01$  mg. The sample is introduced, by means of the capillary and plunger (Fig. 18-52) for solids, or by the use of syringe for liquids, to the bottom of the reaction tube and reweighed. The amount of sample taken should consume 0.1 to 0.2 milli-equivalent of potassium hydroxide. Then exactly 1.00 ml. of 1 N potassium hydroxide in diethylene glycol solution is carefully introduced from a pipet, and the reaction tube is sealed in the oxygen flame. Using the same pipet, exactly 1.00 ml. of the same potassium hydroxide reagent is added to the bottom of a blank tube, which is also sealed.

Both tubes are now placed in the metal block and heated at 150°C. for 2 hr. After cooling to room temperature, the respective tubes are opened. The contents and the sections of the reaction tube and the blank tube are transferred into two 50-ml. Erlenmeyer flasks, each containing 15 ml. of distilled water. Four drops of 0.1% phenolphthalein indicator solution are added to the respective flasks, and the solutions are titrated with standard 0.05 N hydrochloric acid until the pink color disappears. The difference between the titre of the blank and that of the reaction tube gives the amount of potassium hydroxide consumed by the sample.

### MICRODETERMINATION OF THE CARBONYL GROUP BY HYDRAZONE PRECIPITATION

**Principle.**—The carbonyl group is quantitatively precipitated as the 2,4-dinitrophenyl hydrazone of the parent aldehyde or ketone in a suitable medium of controlled pH.



The supernatant liquid is separated by inverted filtration through a filterstick. The precipitate is retained in the reaction vessel, dried and weighed.<sup>48</sup>

<sup>48</sup> Ma, T. S., Logun, J., and Mazzella, P. P., *Microchem. J.*, 1, 67, 1957.

**Apparatus. Reaction Vessel and Filterstick.**—The apparatus for the micro-precipitation and determination of the carbonyl group is shown in Fig. 18-53. A short test tube, of 23-mm. I.D., 100 mm. length, and 35-ml. capacity, serves as the reaction vessel. The filterstick, of 120 mm. length, is prepared from 4-mm. glass tubing (I.D., 2 mm.) by making a capillary constriction about 10 mm. from the

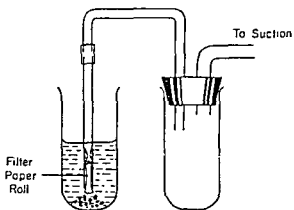


FIG. 18-53. Reaction Vessel and Filterstick.

bottom. The bottom of the filterstick is fitted with a tiny roll of filter paper, the end of which protrudes 1 mm. beyond the filterstick as shown in the figure. The reaction vessel and the filterstick are placed in a 30 ml. beaker, and the 3 pieces are always weighed together.

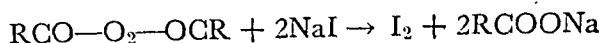
**Procedure. Preparation of the Sample.**—If a double-pan microbalance is used, the dry reaction vessel, filterstick, and beaker are placed on the left pan of the balance. A second beaker and a short test tube of the same dimensions are placed on the right pan, and then lead shots (see Fig. 18-3(b)) are added

into the beaker until the 2 sides are balanced, with the rider sitting between the 0- and 5-mg. marks. After the exact weight has been recorded, the sample is introduced into the reaction vessel. Solid samples are directly added into the reaction vessel with the microspatula. Semi-solids and oils are weighed in a microboat, which is preweighed with the beaker, reaction vessel, and filterstick, and the microboat containing the sample is dropped into the reaction tube after the weighing. Low-boiling liquids are weighed in a microweighing bottle (Fig. 18-13). Five to 15 mg. of the sample (corresponding to between 0.05 and 0.15 milli-equivalent of the carbonyl group) are taken and weighed accurately to  $\pm 0.01$  mg.

**Precipitation, Filtration, and Drying.**—The beaker, containing the sample, filterstick, and reaction vessel, is removed from the balance. Four ml. of methanol are introduced to dissolve the sample. Twenty ml. of the reagent solution (prepared by dissolving 0.2 g. of 2,4-dinitrophenylhydrazine and 1 g. of oxalic acid in 100 ml. of methanol) are added by means of a pipet. The contents of the reaction vessel are thoroughly mixed by gently swirling. Fifteen min. after the appearance of the precipitate, the reaction tube is removed from the beaker and placed in an ice water bath for 1 hr., or until the precipitate settles at the bottom. The reaction vessel is then wiped and returned to the 30-ml. beaker. The filterstick is now connected through a rubber tubing to the siphon, which leads to the filtrate receiver (see Fig. 18-53). The latter consists of a short test tube of 35-ml. capacity, fitted with a 2-holed rubber stopper, with one hole carrying a glass tubing joined to the aspirator. The filterstick is placed inside the reaction tube in such a position that the end of the filter paper roll is just above the precipitate. The supernatant liquid is drawn off by applying slight suction; small amounts of methanol are used to wash the precipitate free of the reagent. When the liquid passing through the siphon becomes colorless, the washing is complete. The precipitate, filterstick, reaction vessel, and beaker are then dried at  $75^{\circ}\text{C.}$  to constant weight.

## MICRODETERMINATION OF THE PEROXY GROUP BY IODINE OXIDATION

**Principle.**—In the presence of ferric ions as catalyst, alkali iodide is readily oxidized by the organic peroxy group to liberate iodine in acetic acid solution.



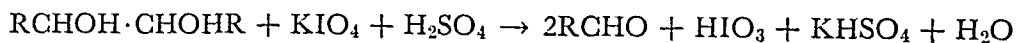
The iodine is then determined by titration with 0.02 *N* sodium thiosulfate solution.<sup>49</sup>

**Apparatus.** Reaction Vessel.—A 50-ml. Erlenmeyer flask, with ground glass stopper, is used as the reaction vessel.

**Procedure.**—Three to 15 mg. of the organic peroxide are weighed accurately into a 50-ml. Erlenmeyer flask provided with glass stopper. Three ml. of chloroform to dissolve the sample are added, followed by 3 ml. of glacial acetic acid containing 0.002% of ferric chloride. The Erlenmeyer flask is flushed with nitrogen while its contents are swirled, and the stopper is replaced immediately. The stopper is then raised sufficiently to permit the addition of 0.15 ml. (3 drops) of saturated aqueous sodium iodide solution from a medicine dropper. The stopper is replaced and again the flask is swirled for complete mixing. After allowing the reaction mixture to stand in darkness for 5 min. at room temperature, 10 ml. of distilled water are added and the iodine liberated is titrated with standardized 0.02 *N* sodium thiosulfate, until the solution lightens to pale yellow. At this point, 1 ml. of starch solution is added and the titration continued to a colorless end point. A blank determination is run using the identical procedure and the same amounts of reagents but without the sample.

## MICRODETERMINATION OF THE ADJACENT DI-OL GROUP BY PERIODATE OXIDATION

**Principle.**—The adjacent di-ol group is specifically oxidized by potassium periodate in dilute sulfuric acid solution.



The sample is treated with a measured amount of the periodate reagent. After the oxidation is completed, the acidic solution is partially neutralized, and a known volume of standardized sodium arsenite solution is added to react with the residual periodate. The excess of arsenite is titrated with 0.025 *N* iodine solution using starch as the indicator.

**Apparatus.** Reaction Flask.—Either a 75-ml. Erlenmeyer flask with ground glass stopper, or 125-ml. iodine flask, may be used as the reaction flask.

**Magnetic Stirrer.**—Any type may be used.

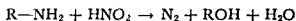
**Procedure.**—Into each of two reaction flasks are added 5.00 ml. of the periodate reagent solution (prepared by dissolving 11.5 g. of potassium meta-periodate in 500 ml. of 0.2 *N* sulfuric acid and diluting to 1 liter). The sample, containing about 0.1 milli-equivalent of the adjacent di-ol group, is accurately weighed into 1 of the 2 reaction flasks, the other flask being used for the blank determination. Both flasks are stoppered and the contents shaken occasionally. After the oxidation is completed (30 min. for simple 1,2-glycols; 1 hr. for monosaccharides; 90 min. for complex glycols), the stopper of the reaction flask is removed, and the magnetic stirring

<sup>49</sup> Ma, T. S., and Gerstein, T., *Microchem. J.*, 5, 163, 1961.

bar is placed in the solution. Five ml. of saturated sodium bicarbonate solution are introduced while the contents of the flask are stirred vigorously. Exactly 10.00 ml. of standardized 0.06 *N* sodium arsenite are added, followed by 0.5 ml. of 20% potassium iodide solution and 2 g. of anhydrous sodium bicarbonate. Both the sample and the blank are allowed to stand for 15 min. with occasional agitation. The starch indicator solution (0.2 ml.) is then introduced and the respective contents of the 2 flasks are titrated with the standardized 0.025 *N* iodine solution while the reaction mixture is stirred magnetically. The end point is the appearance of a faint blue color.

### MICRODETERMINATION OF THE PRIMARY AMINO GROUP BY NITROSATION

**Principle.**—The aliphatic primary amino group reacts with nitrous acid to liberate one mole-equivalent of nitrogen. The latter is collected in a nitrometer and measured.



Nitrous acid is obtained by mixing sodium nitrite with acetic acid; cupric chloride and potassium bromide are added as catalysts for the nitrosation reaction.

**Apparatus.** The Primary Amino Group Assembly.—This is shown in Fig. 18-54. It consists of the carbon dioxide generator, *L*, reaction vessel, *J*, 2 scrubber tubes, *E* and *F*, and the nitrometer, *B*, which has a capacity of 5 ml., and is graduated in 0.02 ml.

**Procedure.** Preparation of the Apparatus and Sample.—The ball-and-socket joints of the assembly are lubricated with a trace of stopcock grease and connected

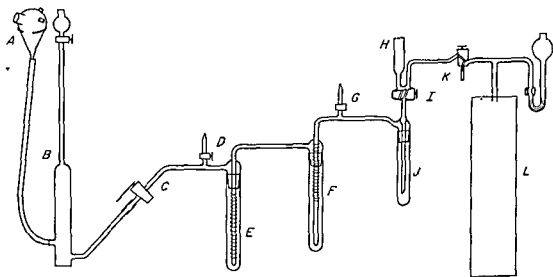


FIG. 18-54. Assembly for Microdetermination of the Primary Amino Group.

as shown in Fig. 18-54. The thermos bottle, *L*, is filled with crushed solid carbon dioxide and the stopcock, *K*, is opened to let carbon dioxide escape to the atmosphere until the carbon dioxide generator is free from trapped air. The nitrometer, *B*, is filled with mercury and 50% potassium hydroxide solution. A pinch of

mercuric oxide and a half-inch flat-headed nail are placed on top of the mercury.

The scrubber tube, *F*, is filled to three-quarters of its length with the potassium bromate reagent solution (prepared by dissolving 5 g. of potassium bromate in 75 ml. of distilled water and diluting with 150 ml. of 50% sulfuric acid). This reagent serves to remove the nitrous oxide produced by the decomposition of nitrous acid.

The scrubber tube, *E*, is filled with a solution of 40% aqueous sodium thiosulfate, which absorbs any bromine produced from the bromate.

The sample containing about 0.1 milli-equivalent of primary amino group is accurately weighed into the reaction vessel, *J*. One ml. of acetic acid-sodium acetate mixture (containing 1 g. of sodium acetate trihydrate in 12.5 ml. of acetic acid and 37.5 ml. of distilled water) is added to the reaction vessel by means of a pipet. The contents of the vessel are mixed by swirling until the sample goes into solution. Then 1 ml. of 10% aqueous potassium bromide solution and 1.5 ml. of 25% cupric chloride solution are added and the neck of the reaction vessel, *J*, is affixed. Twenty ml. of the sodium nitrite reagent solution (1% stock solution diluted with 2 parts of distilled water before use) is delivered into the funnel, *H*.

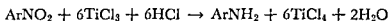
**Purging the Assembly.**—With the leveling bulb, *A*, placed in the lower position to keep the level of potassium hydroxide at the wide part of the nitrometer, the assembly is purged free of air in the following manner: the stopcocks, *C* and *D*, are closed and stopcocks *G*, *I*, and *K* are opened, so that carbon dioxide escapes through *G*. After 2 min., *G* is closed and *D* opened. After 2 more min., *D* is closed and *C* is slowly opened to let carbon dioxide escape through the nitrometer. If the system is free of air, the bubbles forming at the bottom of the nitrometer should practically disappear before they reach the surface of the potassium hydroxide solution. Now the stopcock, *C*, is closed and the leveling bulb, *A*, is raised to fill the nitrometer, *B*, with potassium hydroxide solution. The stopcock on top of the nitrometer is closed and the leveling bulb, *A*, is placed in a position about the middle of the nitrometer. The stopcock, *C*, is then carefully opened so that not more than 3 to 4 bubbles will stay in the whole length of the nitrometer. After 2 min., the nitrosation reaction is ready to proceed.

**Nitrosation.**—The stopcock, *K*, of the carbon dioxide generator is turned to a position so that no gas escapes into the reaction vessel, *J*, or into the atmosphere. Then the stopcock, *I*, above the reaction vessel, *J*, is opened to deliver 1.0 ml. of the sodium nitrite solution into the reaction vessel. Gases are liberated as the nitrosation reaction takes place. The leveling bulb, *A*, is lowered, if necessary, to conduct the gases into the nitrometer smoothly. When no more gas is evolved, 0.2 ml. of the sodium nitrite is introduced into the reaction vessel, *J*, to check if there was sufficient nitrite to react with all the primary amino group.

**Measurement of Nitrogen.**—The stopcock, *C*, is closed and stopcock, *K*, is turned, to allow carbon dioxide to go into the reaction tube, *J*. Now stopcock, *C*, is carefully opened so that a stream of gases goes into the nitrometer. The speed of gas flow is adjusted in such a way that not more than 4 bubbles stay in the nitrometer at one time. When all gas bubbles are absorbed, on rising along the nitrometer, stopcock, *C*, is closed. The leveling bulb is held in a position so that the meniscus of the potassium hydroxide solution in the bulb is at the same level as that inside the nitrometer. Then the volume of gas in the nitrometer is measured, and the room temperature and barometer readings are recorded.

MICRODETERMINATION OF THE NITRO GROUP BY  
REDUCTION WITH TITANOUS CHLORIDE

**Principle.**—The aromatic nitro group is quantitatively reduced by titanous chloride in acid solution.



The sample is treated with a known amount of 0.04 *N* titanous chloride solution. After the reduction is complete, the residual titanous ions are determined by titration with standardized 0.035 *N* ferric alum solution.<sup>50</sup>

**Apparatus.** Apparatus for Titanous Chloride Microtitration.—Because of the susceptibility of titanous chloride to air oxidation, a special assembly is needed for the microdetermination of the nitro group. The apparatus shown in Fig. 18-55

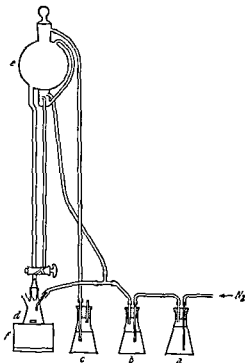


FIG. 18-55. Apparatus for  $\text{TiCl}_3$  Microtitration. (Courtesy Microchim. Acta.)

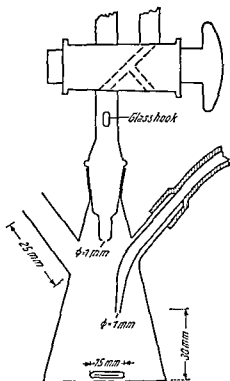


FIG. 18-56. The  $\text{TiCl}_3$  Reaction Flask Connected to the Microburet. (Courtesy Microchim. Acta.)

consists of the nitrogen train *a*, *b*, *c*, reaction flask, *d*, and microburet, *e*. The latter is constructed from a 10 ml. Machlett microburet by replacing its tip with a ground glass joint having a drip tip of 20-mm. length (Fig. 18-56). The 1-liter storage bulb of the microburet is covered with aluminum foil to protect the titanous chloride solution from light.

The reaction flask is constructed from a 50 ml. Erlenmeyer flask having a ground glass joint. It is provided with 2 side arms, each 25 mm. in length. One side arm has an inner diameter of 9 mm. and an outer diameter of 11 mm. Into this side arm is inserted a glass tube having a 4-mm. inside diameter, which is bent so that its tip of 1-mm. inside diameter remains 30 mm. above the bottom of the flask.

<sup>50</sup> Ma, T. S., and Earley, J. V., *Mikrochim. Acta*, 1959, 129.



The other side arm, which serves as outlet for the stream of nitrogen and for adding the reagents, has an inner diameter of 11 mm. and outer diameter of 14 mm. Two springs are used to secure the reaction flask to the buret. A stirring bar of 15-mm. length is placed into the reaction flask.

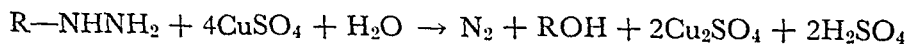
The nitrogen train *a*, *b*, *c*, consists of two 125-ml. Erlenmeyer flasks connected with rubber tubing to a cylinder of nitrogen. Flask *a* contains 1 *N* chromous chloride solution kept over amalgamated zinc; flask *b* contains distilled water. Each flask carries a 2-hole rubber stopper with glass tubing. The tube leading into the chromous chloride solution is drawn out to a fine capillary tip. The flask *c* contains water and is connected with rubber tubing to the side arm of reservoir *e* of the microburet.

**Procedure.**—The nitro compound (3 to 8 mg.) is accurately weighed in the weighing tube (Fig. 18-12) or micro-weighing bottle (Fig. 18-13), and introduced into the reaction flask *d*, which contains 4 ml. of 95% ethanol. The contents of the flask are stirred magnetically until dissolution is complete. The flask is then attached to the microburet (see Fig. 18-55). By means of a pipet, 7 ml. of 2.5 *M* sodium acetate solution are added through the side arm, and the apparatus is flushed with a current of nitrogen for 5 min. at a rate of 20 ml. per min. The 0.04 *N* titanous chloride solution is then added from the microburet until the color of the reaction mixture changes to deep violet. After 3 min., 4 ml. of concentrated hydrochloric acid are added, and the contents of the reaction flask are titrated with the standardized 0.035 *N* ferric alum solution delivered from a 5-ml. microburet until the pale blue color of titanous chloride almost disappears. Two ml. of 2.5 *M* ammonium thiocyanate indicator solution are now introduced and the titration is continued. The end point is the appearance of a pink color that persists for 1 min.

A blank is performed with the same procedure and quantities of reagent as used in the analysis of the sample.

## MICRODETERMINATION OF THE HYDRAZINO GROUP BY MILD OXIDATION

**Principle.**—The hydrazino group in many compounds can be decomposed with a mild oxidizing reagent, such as copper sulfate, to yield nitrogen gas.



Heating is usually required to bring the oxidation to completion. The nitrogen liberated is collected and measured in a nitrometer.

**Apparatus.** The Micro Hydrazino Apparatus.—As shown in Fig. 18-57, the micro hydrazino apparatus consists of the reaction vessel, *A*, reflux condenser, *E*, and the 5-ml. nitrometer, *FG*. The side arm, *B*, of the reaction vessel is fitted with a rubber stopper of sleeve type. The sleeve can be folded down over the neck of the side arm. The diaphragm of the stopper can be punctured readily with a syringe needle, and the puncture seals automatically after the needle is withdrawn.

**Procedure.**—The rubber stopper, *D*, is removed for the introduction of the sample, containing about 0.1 milli-equivalent of hydrazino group, into the reaction vessel, *A*, through the side arm, *B*. Two ml. of a suitable solvent (water, dilute sulfuric acid, or glacial acetic acid) are added. The stopcock of the carbon dioxide generator (not shown) is opened to purge the reaction vessel, *A*, free from air. Then the rubber stopper is replaced and the current of carbon dioxide is continued, to expel all air out of the apparatus (for checking the system, see "Micro-determination of the Primary Amino Group by Nitrosation," above, p. 413). The

nitrometer is now filled with potassium hydroxide solution, and the stopcock of the carbon dioxide generator is turned off.

Using a syringe with a long needle, 4.0 ml. of saturated aqueous solution of copper sulfate are introduced through the diaphragm of the rubber stopper. The

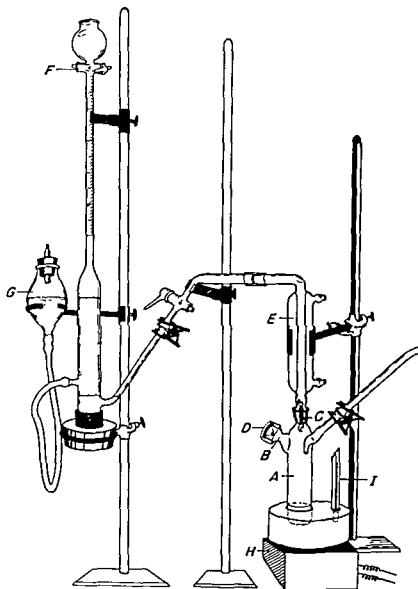


FIG. 18-57. Apparatus for Microdetermination of Hydrazino Group.

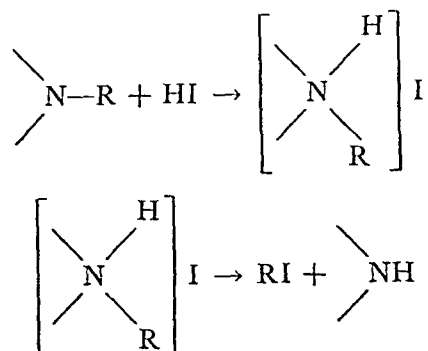
heating stage, *H*, is turned on gradually to raise the temperature of the reaction mixture. Gas bubbles enter the nitrometer due to expansion of gas volume by heat and also, to the liberation of nitrogen from the hydrazino group. The speed of the gas entering the nitrometer is controlled by adjusting the stopcock on the delivery tube leading to the nitrometer. If the gas flow stops, the stopcock of the carbon dioxide generator is carefully opened to maintain the gas speed.

When the contents of the reaction vessel, *A*, begin to boil, the heating stage is switched off. The reaction vessel, *A*, is kept in the hole of the heating stage for

10 min. longer before the latter is removed. When all the nitrogen produced has been driven into the nitrometer, the volumes of gas, temperature, and atmospheric pressure are noted. The heating stage is replaced under the reaction vessel, *A*, to boil the reaction mixture for 5 min. while a slow current of carbon dioxide passes through. Heating is continued if more nitrogen is produced.

### MICRODETERMINATION OF THE ALKIMINO GROUP

**Principle.**—The alkimino group forms quaternary ammonium iodide upon heating with concentrated hydriodic acid. When the quaternary ammonium salt is pyrolyzed, one mole-equivalent of alkyl iodide is liberated



The microdetermination of the alkimino group is based on the volatility of the resulting alkyl iodide. Therefore, this method is best suited for the analysis of the methylimino and ethylimino groups. The methyl or ethyl iodide produced is converted to silver iodide and weighed.

**Apparatus.** *Modified Friedrich Alkimino Apparatus.*—The Friedrich apparatus<sup>51</sup> for microdetermination of the methyl- or ethylimino group is modified as shown in Fig. 18-58 to increase the flexibility of the assembly and to permit the addition of fresh hydriodic acid into the reaction mixture. The reaction vessel, *A*, is provided with a side tube for admitting nitrogen gas, and a ground glass joint for the passage of gas stream into the condenser tube, *D*, through the scrubber, *F*, into the receiver *H*. The stopcocked funnel, *B*, serves as reservoir for hydriodic acid.

**Procedure.**—The scrubber tube, *F*, is filled with a solution containing equal volumes of 5% cadmium sulfate and 5% sodium thiosulfate, and closed with a cork. The receiver tube, *H*, is charged with 2 ml. of 4% ethanolic silver nitrate solution. The sample (5 to 10 mg.) is accurately weighed, by means of the weighing tube or micro weighing bottle, into the reaction vessel, *A*, through the side arm with ground-glass joint. The sample is dissolved in a few drops of propionic anhydride. Ammonium iodide crystals, equal to about 20 times the weight of the sample, are added. The reaction vessel, *A*, is then connected to the bent tube, *C*. The condenser tube, *D*, is immersed in a beaker of water kept at 90°C.

A slow stream of nitrogen gas is passed through the apparatus in such a manner that not more than 2 bubbles remain in the receiver at one time. About 2 ml. of hydriodic acid (sp. gr. 1.7) are introduced from the reservoir funnel, *B*. The contents of the reaction vessel, *A*, are now kept at gentle boiling (or preferably placed in the heating stage maintained at 120°C.) for 30 min. Then the reaction vessel, *A*, is placed in a sand bath (or in the heating stage), which is gradually heated to

<sup>51</sup> Friedrich, A., *Mikrochemie*, 1, 185, 1929; *Die Praxis der quantitativen organischen Mikroanalyse* Deuticke, Wien, 1933.

360°C. The hydriodic acid distils and condenses in the condenser tube, *D*, while the alkyl iodide passed through the stopcock, *E*, and scrubber tube, *F*, into the receiver, *H*. The dry residue in the reaction vessel, *A*, is heated at 360°C. for 5 min. Then the temperature of the bath is lowered to 100°C. A second batch of hydriodic acid is delivered from the reservoir and the process is repeated.

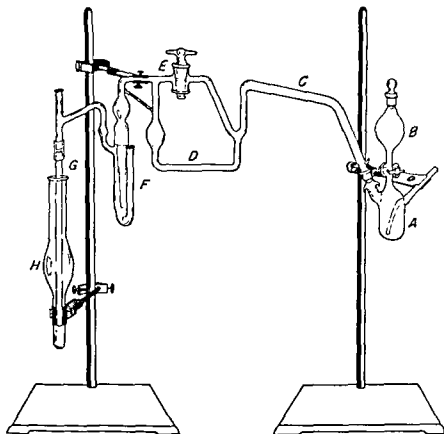
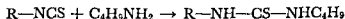
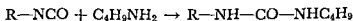


FIG. 18-58. Modified Friedrich Apparatus for the Microdetermination of Alkyl Iodide.

After the collection of methyl or ethyl iodide in the receiver tube is completed, the receiver tube, *H*, is disconnected at the rubber connection, *G*. The delivery tube is rinsed with dilute nitric acid. The silver iodide in the receiver is coagulated by heating in a water bath, transferred onto a filter tube (see "Gravimetric Determination of Chloride or Bromide," above, p. 398), dried at 105°C., and weighed.

### MICRODETERMINATION OF ISOCYANATE AND ISOTHIOCYANATE GROUPS

**Principle.**—The isocyanate and isothiocyanate groups are determined by treatment with an excess of *n*-butylamine in dioxane to form the corresponding substituted urea and thiourea, respectively.



The excess of butylamine is then determined by titration with standard 0.02 *N* hydrochloric acid.<sup>52</sup>

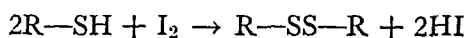
*Apparatus.*—Iodine flask, 125-ml. capacity. Magnetic stirrer.

*Procedure.*—The reaction vessel is assembled by placing a stirring bar into the 125-ml. iodine flask, adding 10 ml. of the *n*-butylamine reagent solution (prepared by dissolving 2 g. of *n*-butylamine in 1 liter of *p*-dioxane) from a pipet, and replacing the stopper. The sample containing about 0.1 milliequivalent of isocyanate group is delivered into the microweighing bottle (Fig. 18-13) by means of a dropper with a capillary tip, and accurately weighed. The microweighing bottle and sample are dropped into the reaction vessel, which is then placed on the magnetic stirring device. After the reaction vessel stopper is replaced, the magnetic stirrer is switched on. The stirring of the contents is usually sufficient to open the microweighing bottle. If necessary, a glass hook can be used to catch the eye on the microweighing bottle stopper to disengage the latter; the hook can be broken in the reaction vessel and left there.

After the reaction mixture is stirred for 1 min., it is allowed to stand 15 min. for aromatic isocyanates or isothiocyanates, and 45 min. for aliphatic compounds. Then 20 ml. of distilled water are introduced to the well of the iodine flask and the stopper is opened. After adding 2 drops of 0.1% ethanolic methyl red solution as indicator, the contents of the flask are titrated with standardized 0.02 *N* hydrochloric acid to a distinct pink end point. A blank is run on 10 ml. of the *n*-butylamine reagent solution under identical conditions.

### MICRODETERMINATION OF THE SULFHYDRYL GROUP BY OXIDATION WITH IODINE

*Principle.*—The sulfhydryl group can be determined by oxidation with iodine.



A standard solution of iodine is not suitable for microanalysis, however, because it is very unstable. An indirect method is therefore employed. The compound containing the sulfhydryl group is mixed with potassium iodide in glacial acetic acid solution. The mixture is then titrated with the standardized 0.03 *N* potassium iodate solution. Iodine, which is produced by the reaction between iodide and iodate, is immediately consumed by the sulfhydryl group. The end point is the appearance of iodine color in the solution.

*Apparatus.*—No special apparatus is required.

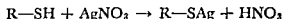
*Procedure.*—A sample containing about 0.1 milliequivalent of the sulfhydryl group is accurately weighed into a 50-ml. Erlenmeyer flask. Five ml. of methanol are added to dissolve the sample, followed by 1 ml. of glacial acetic acid, 400 mg. of potassium iodide, and 1 ml. of distilled water. The flask is swirled until all solids have dissolved. The solution is then titrated with the standardized 0.03 *N* potassium iodate solution until the appearance of the yellow color of free iodine, which persists for 30 sec.

### MICRODETERMINATION OF THE SULFHYDRYL GROUP BY AMPEROMETRIC TITRATION WITH SILVER NITRATE

*Principle.*—Another micromethod for the determination of the sulfhydryl group is dependent on the precipitation of silver mercaptide in aqueous or

<sup>52</sup> Karten, B., and Ma, T. S., *Microchem. J.*, 3, 507, 1959.

ethanolic solution.



The end point of the reaction is located amperometrically.

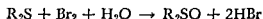
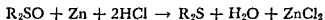
**Apparatus.** Amperometric Titration Assembly.—The various parts of the amperometric microtitration assembly are shown in Fig. 18-59.

**Polarograph.**—Any type.

**Procedure.**—Approximately 0.1 milliequivalent of the sulfhydryl compound is accurately weighed into a 100-ml. beaker and dissolved in 5 ml. of 95% ethanol. Twenty-five ml. of buffer solution, containing 0.25 *M* ammonium nitrate and 1 *M* ammonium hydroxide, are added, followed by 1 ml. of 0.01% gelatin in ethanol. The stirring bar is placed in the beaker and the apparatus is assembled as shown in Fig. 18-59. A stream of nitrogen is passed through the solution to expel the absorbed oxygen. The magnetic stirrer is switched on and the dropping mercury electrode is lowered into the solution, while a steady flow (drop by drop) of mercury takes place inside the solution, the calomel cell-glass electrode is immersed in the solution, and the leads are connected to the polarograph. The standardized 0.01 *N* silver nitrate solution is slowly delivered from the microburet. The reading of the polarograph after each increment of the titrant is noted. The titration is continued until significant increases in the current are observed. The equivalence point is obtained by plotting the current-volume curve.

### MICRODETERMINATION OF THE SULFOXIDE GROUP

**Principle.**—The sulfoxide group can be determined on the micro scale by quantitative reduction with amalgamated zinc and hydrochloric acid to yield the corresponding sulfide, and the subsequent determination of organic sulfide by oxidation with bromine.



The reduction process is carried out in a micro-Jones reductor. Because of the instability of free bromine, a mixture of bromate and bromide is used as the standard solution of bromine.

**Apparatus.** Micro-Jones Reductor.—As shown in Fig. 18-60, the micro-Jones reductor consists of 2 U-tubes, connected by ground-glass joints. One U-tube contains the funnel, *A*, and the reducing column, *E*, which holds the zinc amalgam. the other U-tube, *FG*, acts as a spigot.

**Procedure.** Preparation of the Assembly.—In a 250-ml. beaker are placed 100 g. of 20-mesh zinc metal. One hundred ml. of 2 *N* hydrochloric acid are added and the contents of the beaker stirred for 1 min. to etch the surface of the zinc. A freshly prepared solution containing 400 mg. of mercuric chloride in 50 ml. of 1 *N* hydrochloric acid is introduced, and the mixture is stirred for 5 min. Then the supernatant liquid is decanted off and the amalgamated zinc is washed several times by water and decantation.

A wad of glass wool, *D*, is inserted into the reducing column, *E*, of the micro-Jones reductor. The amalgamated zinc is now transferred into the column and packed loosely by gentle tapping. Another wad of glass wool is placed above the zinc and the column is washed with distilled water several times, once with 10% acetic acid, and finally with a 5% hydrochloric acid in 95% ethanol.

*Preparation of the Sample and Reduction.*—A sample containing about 0.1 milliequivalent of the sulfoxide group is accurately weighed into a 10-ml. micro-Kjeldahl digestion flask (see "Microdetermination of Nitrogen by the Kjeldahl Principle,"

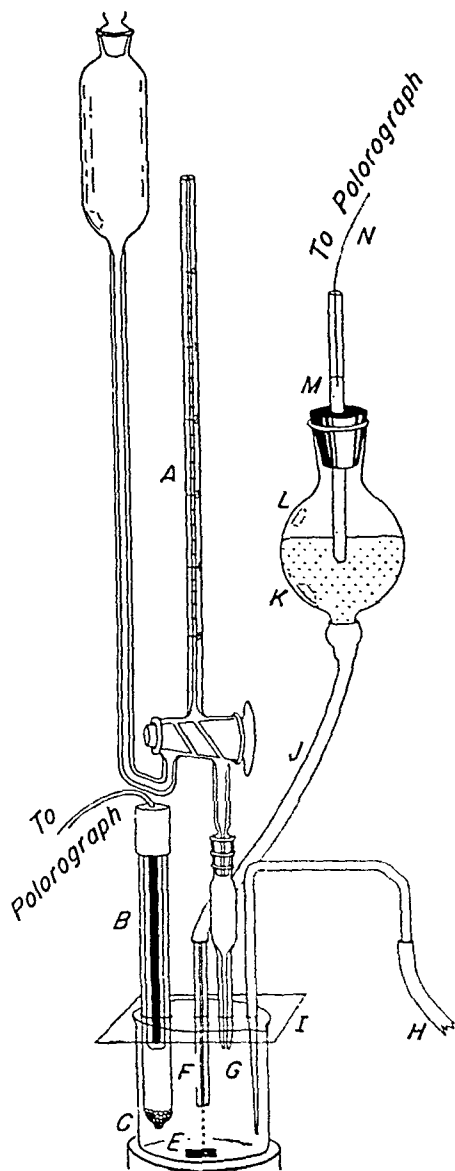


FIG. 18-59. Amperometric Titration Assembly for Microdetermination of the Sulfhydryl Function.

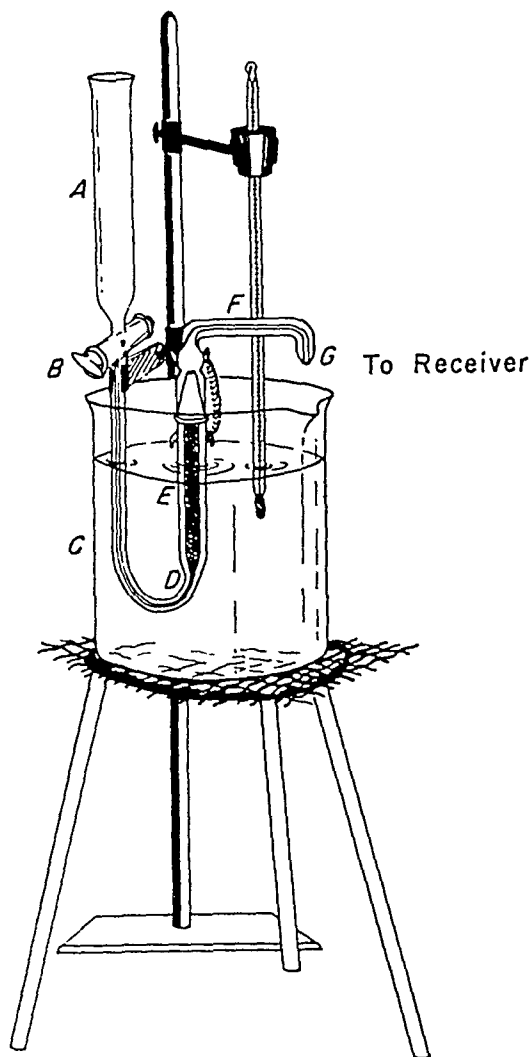


FIG. 18-60. Micro Jones Reductor.

above, p. 384). Five ml. of 5% ethanolic hydrochloric acid are added to dissolve the sample by swirling. A trace of vaseline is smeared on the lip of the digestion flask. With the reducing column of the micro-Jones reductor immersed in a water bath at 50°C., and the stopcock, *B*, closed, the contents of the digestion flask are transferred into the funnel, *A*. Then the stopcock, *B*, is turned to allow the solu-

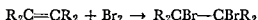
tion to move down through the U-tube in such speed that the liquid front travels through the entire length of the reducing column, *E*, in 10 min. The effluent is collected in a 125-ml. iodine flask. The digestion flask is rinsed with 5 ml. of 5% ethanolic hydrochloric acid and the rinsing is transferred into the funnel, *A*. Finally, 40 ml. of glacial acetic acid are introduced into the funnel and collected in the 125-ml. iodine flask.

**Microdetermination of Aliphatic Sulfide.**—If aliphatic sulfide is collected in the 125-ml. iodine flask, 1.5 ml. of concentrated hydrochloric acid are introduced, followed by a solution containing 500 mg. of potassium bromide in 2 ml. of distilled water. The iodine flask is closed and its contents mixed by swirling. After 5 min., the solution is titrated with the standardized 0.07 *N* potassium bromate solution. The end point is the appearance of bromine color which persists for 30 sec.

**Microdetermination of Aromatic Sulfide.**—If the 125-ml. iodine flask contains aromatic sulfide, 2.0 ml. of concentrated hydrochloric acid are added. Then exactly 5.00 ml. of the standardized 0.1 *N* potassium bromate solution are delivered into the iodine flask. The stopper is replaced and the flask is swirled to mix the contents. Now 500 mg. of potassium bromide are added. The flask is again closed and shaken for 1 min. Then the flask is placed in a water bath at 60°C. for 2 min. After cooling to room temperature, 2 ml. of 15% potassium iodide solution are added, and the stoppered flask is shaken for 1 min. The contents of the flask are titrated with the standardized 0.1 *N* sodium thiosulfate solution, using starch as indicator. A blank is run using identical amounts of the reagents.

### MICRODETERMINATION OF THE UNSATURATED GROUP BY BROMINE ADDITION

**Principle.**—The unsaturated group in olefins can be determined by the addition of bromine.



Because of the difficulty in handling standardized bromine solution for microanalysis, the reagent is generated *in situ* by action of bromate on bromide ions in the presence of hydrochloric acid.

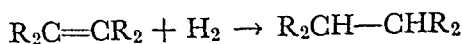
**Apparatus.** Reaction Vessel.—A 50-ml. Erlenmeyer flask, provided with ground glass stopper, is used as the reaction vessel.

**Procedure.**—In the reaction vessel are placed 10 ml. of the solvent mixture, which is prepared by combining 714 ml. of glacial acetic acid, 134 ml. of carbon tetrachloride, 116 ml. of methanol, 18 ml. of dilute sulfuric acid (1:5 v/v) and 18 ml. of 10% methanolic solution of mercuric chloride. The sample containing about 0.1 milliequivalent of unsaturated group is then accurately weighed and added into the reaction vessel. After cooling the reaction mixture for 5 min. in the ice water bath, 0.25 ml. of concentrated hydrochloric acid is added. The contents of the flask are now titrated with the standardized 0.05 *N* bromate-bromide reagent (containing 1.392 g. of potassium bromate and 5.0 g. of potassium bromide in 1 liter). The end point is the appearance of a yellowish tinge which persists on swirling for 30 sec. A blank is performed along with the sample and titrated in the same fashion.



# MICRODETERMINATION OF THE UNSATURATED GROUP BY HYDROGENATION

**Principle.**—Another micromethod for the determination of the unsaturated group involves the measurement of the volume of hydrogen consumed by the sample.



A catalyst is needed for the reaction to proceed at a reasonable rate. Sometimes the reaction goes to completion only at an elevated temperature.

**Apparatus. Micro Gasometric Apparatus.**—The versatile apparatus for micro gasometric analysis, according to Ma and Scheinthal, is shown in Fig. 18-61. It

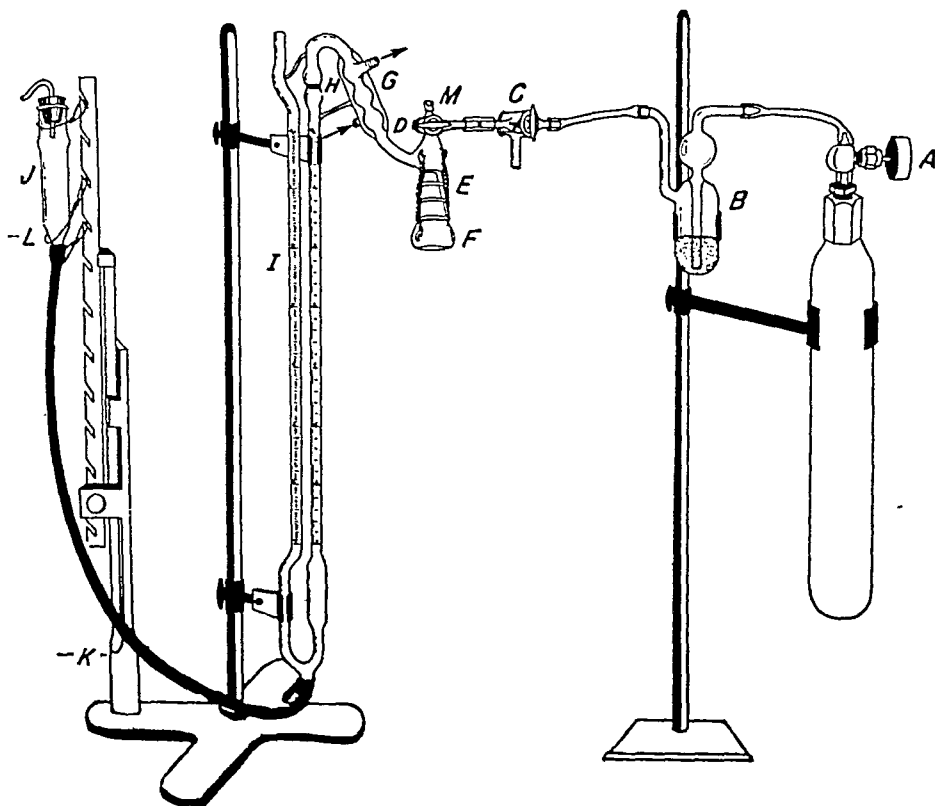


FIG. 18-61. Micro Gasometric Apparatus of Ma and Scheinthal. (Reprinted with permission from Cheronis, N. D., *Microchemical Techniques*, John Wiley and Sons, Inc., New York, 1962.)

consists of a lecture gas cylinder with needle valve, *A*, bubble counter, *B*, 3-way stopcock, *C*, reaction chamber, *DEFG*, gas buret, *HI*, and leveling bulb, *J*. The reaction vessel, *F*, is connected to the cap, *E*, by means of springs. The condenser, *G*, permits the reaction to be performed at the boiling point of the solvent used in the determination. A sintered glass disc is sealed on top of the gas buret in order to prevent the mercury from entering the condenser. One end of the 3-way stopcock is fitted with a rubber syringe cap, *M*.

**Heating and Stirring Device.**—The controlled temperature bath which is used with the micro gasometric apparatus is shown in Fig. 18-62. It consists of a large U-tube with a flat bottom. The heating unit, *IH*, is immersed in one side, while

the reaction flask, *C*, is placed in the other side. *AB* is a magnetic stirrer constructed from a toy motor attached to the magnet, *B*. A stirring bar, *G*, is placed at the bottom of the U-tube so that the bath fluid may be stirred if necessary.

**Procedure. Preparation of the Apparatus and Sample.**—Into the reaction flask, *F* (Fig. 18-61), are placed 300 to 500 mg. of the catalyst (platinum black, Raney nickel, etc.), 3 ml. of the solvent (e.g., dioxane, glacial acetic acid), and 2 to 3 micro stirring bars. The neck of the reaction flask is lubricated with stopcock grease and the apparatus is assembled as shown in Fig. 18-61.

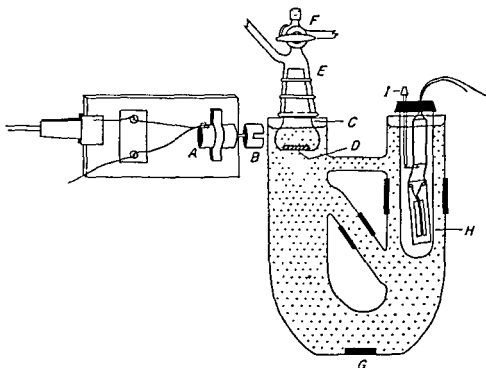


FIG 18-62. Heating and Stirring Device for the Micro Gasometric Apparatus.

The apparatus is purged free of air as follows: the leveling bulb, *J*, is lowered to position, *K*; the needle valve, *A*, of the hydrogen cylinder is opened to pass a stream of hydrogen through the system; the gas flow is adjusted so that gas bubbles through the bubble counter, *B*, at a moderate rate and a mercury seal is maintained in the gas buret, *I*, at level, *K*. After 5 min., the open end of the 3-way stopcock, *C*, is connected to the water aspirator. The leveling bulb, *J*, is raised to position *L* and the stopcock, *C*, is momentarily turned to connect the apparatus to the vacuum line. After about 20 sec., the stopcock, *C*, is again returned to the hydrogen line and the leveling bulb to position *K*. The above operation is repeated twice. The leveling bulb, *J*, is then placed at position *L*, and hydrogen gas is passed in to push the mercury back so that the 2 columns of mercury in the gas buret, *HI*, are at the same level, *L*. The stopcock, *D* (above the reaction flask cap, *E*), is turned so that no more hydrogen enters the reaction flask, and the 3-way stopcock, *C*, is turned to let excess hydrogen escape to the atmosphere. Then the needle valve, *A*, of the gas cylinder is shut off. The readings of volume, temperature, and atmospheric pressure are noted.

An accurately weighed sample is placed in a 10-ml. volumetric flask and dis-

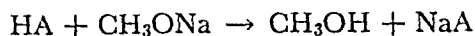
solved in a suitable solvent. Using a syringe with long needle, an aliquot containing about 0.1 milliequivalent of the unsaturated group is delivered into the reaction flask, *F*, through the cap, *E*. All stopcocks are turned to give a closed system.

**Hydrogenation.**—The magnetic stirrer is switched on. As hydrogenation proceeds, the leveling bulb, *J*, is gradually raised to maintain a pressure of 30 mm. mercury on the system. When there is no change in the volume of gas in the gas buret, *HI*, for 5 min., the magnetic stirrer is switched off. The leveling bulb, *J*, is adjusted so that the 2 mercury columns are again at exactly the same level. The volume, temperature, and barometer readings are recorded.

A blank is run using the same amounts of reagents and conditions.

### MICRODETERMINATION OF ACIDIC GROUPS BY NONAQUEOUS TITRATION

**Principle.**—Phenols, sulfonamides, barbiturates, enols, imides, and some hydrazides can be determined on the micro scale as acids. The sample is dissolved in dimethylformamide and titrated with 0.02 *N* sodium methoxide.<sup>53</sup>



The end point may be located visually or potentiometrically. As carbon dioxide interferes with the analysis, its presence cannot be tolerated.

**Apparatus. Titration Assembly.**—In order to minimize the absorption and consequent interference of carbon dioxide from the air, the titration assembly shown in Fig. 18-63 is recommended. The microtitration vessel is essentially a small Florence flask with a capacity of about 50 ml., that has 5 necks, 1 in line with the vertical axis of the vessel and the other 4 equally spaced, slightly oblique, and lower. The vertical neck has a ground-glass joint which accommodates the tip of the microburet. Two diametrically opposed side openings are 10 mm. in diameter to allow insertion of electrodes. The other two openings permit a continuous flushing with nitrogen gas. The capillary tube ends about 3 mm. from the bottom of the vessel.

**Procedure. For Visual Titration.**—Five ml. of dimethylformamide are introduced into the microtitration vessel through the 10-mm. side neck. The 2 side necks allocated for electrodes are closed and the flow of nitrogen is adjusted so that individual bubbles can be seen. The magnetic stirrer is switched on so that agitation is rapid but spattering does not occur. The indicator solution (0.03 ml. of 0.3% thymol blue or 0.015 ml. of 0.5% azo-violet) is added, and the acid impurities in the solvent are neutralized by adding standardized 0.02 *N* sodium methoxide in benzene-methanol, until a permanent blue color appears. Now the sample containing about 0.1 milliequivalent of the acidic group is accurately weighed by means of the weighing tube (Fig. 18-12), and introduced into the titration vessel through the side neck. After the sample dissolves, the solution is titrated to the blue end point.

**For Potentiometric Titration.**—Into the microtitration vessel are added 15 ml. of dimethylformamide. The flow of nitrogen and stirring are regulated as described above. The electrodes are inserted in their appropriate locations, one facing the other, so that they are at least 2 mm. below the surface of the liquid, and are separated by a distance of less than 5 mm. The sample is now introduced

<sup>53</sup> Maurmeyer, R. K., Margosis, M., and Ma, T. S., *Mikrochim. Acta*, 1959, 177.

through the side neck. With the potentiometer properly connected and set, the titration with the standardized 0.02 *N* sodium methoxide is started with large increments of titrant. The volume is reduced when approaching the equivalence point. The titration is continued until the equivalence point is well passed.

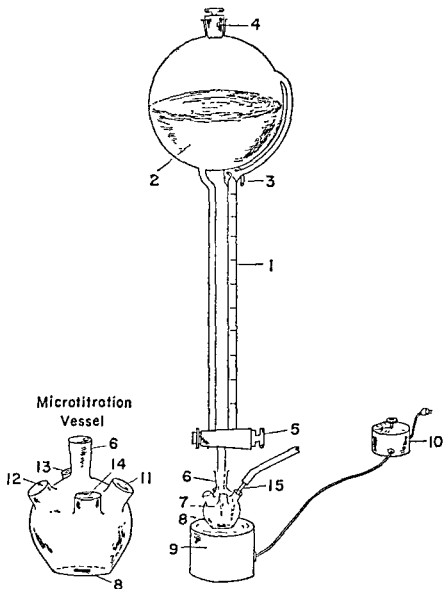
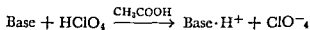


FIG. 18-63. Apparatus for Microdetermination of Very Weak Acids. (Courtesy Mikrochim. Acta)

### MICRODETERMINATION OF BASIC GROUPS BY NONAQUEOUS TITRATION

**Principle.**—Organic bases with  $pK_b$  values in water up to 12 can be determined on the micro scale by titration against 0.01 *N* perchloric acid using dioxane, chloroform, and acetic acid as the mixed solvent.<sup>54</sup>



The equivalence point may be located visually or potentiometrically.

<sup>54</sup> Gutterson, M., and Ma, T. S., Mikrochim. Acta, 1960, 1.

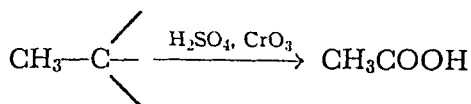
**Apparatus.**—No special apparatus is required.

**Procedure. For Visual Titration.**—The sample, containing about 0.1 milliequivalent of the basic group, is accurately weighed into a 125-ml. Erlenmeyer flask. Ten ml. of glacial acetic acid are added. If the sample does not dissolve readily on swirling the flask, the latter may be placed on a hot plate to effect complete dissolution. After cooling to room temperature, 30 ml. of chloroform and 0.1 ml. of 0.1% crystal violet indicator solution are added. The contents of the Erlenmeyer flask are then titrated with the standardized 0.01 *N* perchloric acid in dioxane, until the solution changes from violet to blue. A blank is performed using the same procedure and equal amounts of reagents.

**For Potentiometric Titration.**—About 0.1 milliequivalent of the sample is accurately weighed into a 100-ml. beaker containing a magnetic stirring bar. Ten ml. of glacial acetic acid are added to dissolve the sample, and the mixture is heated on a hot plate, if necessary. After cooling, 20 ml. of chloroform are added, and the electrodes are immersed into the solution. The magnetic stirrer is switched on and the standard 0.01 *N* perchloric acid in dioxane is delivered into the beaker from the microburet. The potential reading after each increment of the titrant is noted. The increments near the equivalence point should be 0.02 to 0.05 ml. The titration is continued until the equivalence point is well passed. The equivalence point is determined graphically.

### MICRODETERMINATION OF THE C-METHYL GROUP<sup>55</sup>

**Principle.**—The methyl group attached to the carbon atom in certain structures (e.g., isoprene) can be quantitatively oxidized to yield one mole-equivalent of acetic acid. The oxidizing agent used is a mixture of chromic acid and sulfuric acid, and the reaction is performed in the sealed tube.



After the oxidation, the acetic acid is separated by steam distillation and determined by titration with 0.01 *N* sodium hydroxide.

**Apparatus. Reaction Tube.**—The reaction tube is prepared from 8-mm. glass tubing using the technique previously described in "Microdetermination of the Hydroxyl Group by Acetylation," above, p. 405.

**Heating Device.**—A sand bath placed on a rocking machine may be used. The rocking furnace of Tashinian, Baker, and Koch<sup>55</sup> (Fig. 18-64) is recommended for routine determinations.

**Steam Distillation Apparatus.**—The steam distillation apparatus is shown in Fig. 18-65. It consists of the steam generator, *A*, trap, *B*, distilling flask, *D*, and condenser, *E*.

**Procedure. Preparation of the Sample and Oxidation.**—The sample, containing about 0.1 milliequivalent of C-methyl group, is accurately weighed into the reaction tube. Two ml. of concentrated sulfuric acid are added as solvent. The solution is then cooled in the ice bath and 4 ml. of 5 *N* chromic acid are carefully introduced into the reaction tube by means of a pipet. After sealing, the reaction tube is placed in the heating device where the temperature is gradually raised to 110°C. and maintained for 1 hr.

<sup>55</sup> Tashinian, V. H., Baker, M. J., and Koch, C. W., *Anal. Chem.*, 28, 1304, 1956.

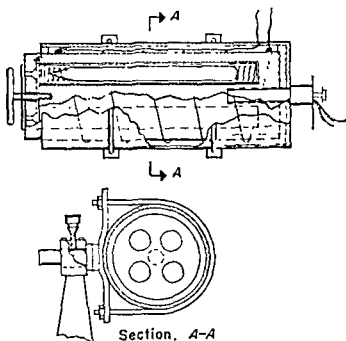


FIG. 18-64. Rocking Furnace for Microdetermination of C-Methyl Group.  
(Courtesy Anal. Chem.)

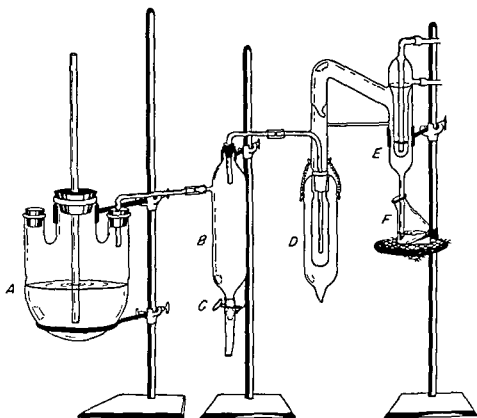


FIG. 18-65. Steam Distillation Apparatus. (Reprinted with permission from Microchemical Journal, 4, 484, 1960, John Wiley and Sons, Inc., New York.)

**Distillation and Titration.**—The sealed tube is allowed to cool to room temperature. The tip is then opened with a flame to release the pressure, and the tube is cut as previously described. The contents of the reaction tube are quantitatively transferred into the distilling flask, *D* (Fig. 18-65). A 250-ml. Erlenmeyer flask is placed under the condenser, *E*. Steam is passed into the distilling flask, *D*, and 100 ml. of distillate are collected.

Three drops of 1% phenolphthalein indicator solution are added to the distillate, which is titrated with standard 0.01 *N* sodium hydroxide. The end point is a pink color which persists for 30 sec.

## MICRO GRAVIMETRIC INORGANIC ANALYSIS

### MICRODETERMINATION OF SODIUM AS SODIUM-ZINC-URANYL ACETATE

**Principle.**—Sodium can be determined on the milligram scale by precipitation in form of sodium-zinc-uranyl acetate  $\text{NaZn}(\text{UO}_2)_3(\text{CH}_3\text{COO})_9 \cdot 9\text{H}_2\text{O}$ . Because the precipitate is significantly soluble in water, a concentrated solution of the reagent is used, and the product is washed with the reagent solution, followed by alcohol and ether.

**Apparatus.**—Porcelain crucible and filterstick (see Fig. 18-44).

**Procedure. Preparation of the Reagent.**—A solution containing 6 g. of zinc acetate trihydrate, 0.2 ml. of glacial acetic acid, and 10 ml. of distilled water, and another solution containing 2 g. of uranyl acetate dihydrate, 0.4 ml. of glacial acetic acid, and 10 ml. of distilled water are separately prepared. Ten ml. of each solution are combined, thoroughly mixed and allowed to stand for 2 days before use.

**Precipitation and Determination.**—Into the crucible (previously weighed with the filterstick) is added the sample containing 0.3 to 1 mg. of sodium. Solid substance is introduced by means of the weighing tube (Fig. 18-12). Solution is introduced by a transfer pipet and then evaporated to dryness. The sample is dissolved in 0.15 to 0.25 ml. of distilled water, and 10 times the volume of the zinc uranyl acetate reagent solution are introduced in the following manner: a graduated pipet is connected to a glass tubing with constriction, and holding a filter paper roll as shown in Fig. 18-66; the glass tubing and filter paper are dipped into the zinc uranyl reagent solution and a suitable volume is sucked into the buret; then the buret is lifted up, the filter paper roll is discarded, and the required volume is delivered into the crucible.

The reaction mixture is allowed to stand for 1 hr. The filterstick is placed in position and the supernatant liquid is removed by inverted filtration. The precipitate is washed 3 times with 95% ethanol and once with diethyl ether. The crucible and its contents are dried in a vacuum desiccator for 15 min. and weighed.

### MICRODETERMINATION OF ALUMINUM AS OXINATE

**Principle.**—The aluminum compound is dissolved in dilute hydrochloric acid, and an excess of 8-hydroxyquinoline reagent is added. The reaction mixture is neu-

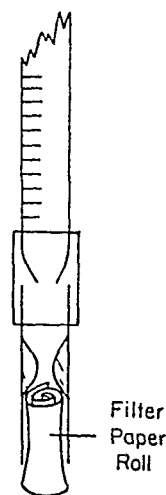


FIG. 18-66. Buret Attachment for Filtration of Reagent Solution.

tralized with ammonium acetate to produce a quantitative precipitation of the chelate compound, aluminum oxinate. The precipitate is freed from the mother liquor, washed, dried at  $140^{\circ}\text{C}.$ , and weighed. One mg. of aluminum oxinate contains 0.0587 mg. of aluminum.

**Apparatus.** Reaction Tube and Filterstick.—The assembly shown in Fig. 18-53 (see "Microdetermination of the Carbonyl Group by Hydrazone Precipitation," p. 410) is used. The reaction tube need not have a capacity greater than 15 ml.

**Procedure.**—The sample containing about 0.5 mg. of aluminum is accurately weighed into the reaction vessel and dissolved in a minimum volume of 0.2 *N* hydrochloric acid. The reaction vessel may be heated at  $100^{\circ}\text{C}.$  to facilitate dissolution of the sample. Into the reaction vessel is then delivered 1 ml. of the oxine reagent (2% hydroxyquinoline in 1 *N* acetic acid). After keeping the reaction mixture at  $100^{\circ}\text{C}.$  for 2 min., 2 *N* ammonium acetate solution is added until a cloudiness is produced. Heating is continued for 2 to 3 min. until the precipitate begins to coagulate. Now 1 ml. more of 2 *N* ammonium acetate is added, followed by a few drops of the oxine reagent to test for complete precipitation. After 10 min. the reaction vessel is removed from the heating bath. The mother liquor is filtered off and the precipitate is washed 5 times with 1-ml. portions of distilled water. The reaction vessel and its contents are dried at  $140^{\circ}\text{C}.$  for 30 min., cooled to room temperature, and weighed.

## MICRODETERMINATION OF CALCIUM AND MAGNESIUM IN LIMESTONE

**Principle.**—The limestone sample is fused with sodium carbonate-potassium carbonate mixture. The fusion is treated with hydrochloric acid. After the removal of silica, the solution is made alkaline to precipitate iron and aluminum hydroxides. Calcium is determined in the filtrate as the oxalate monohydrate. After the separation of calcium, magnesium is precipitated in the form of magnesium ammonium phosphate hexahydrate and weighed as such.<sup>56</sup>

**Apparatus.** Platinum Crucible.—Crucible, 15-ml. capacity, with lid.

**Reaction Tube and Filterstick.**—See "Microdetermination of the Carbonyl Group by Hydrazone Precipitation," above, p. 410.

**Micro Water Bath.**—This is constructed from an Erlenmeyer flask and adapter as shown in Fig. 18-67.

**Procedure.** Preparation of the Sample and Fusion.—The limestone is finely ground in an agate mortar, screened through the micro sieve (Fig. 18-9), and a representative sample is obtained by quartering. About 5 mg. of the sample are accurately weighed into the platinum crucible by means of the micro-weighing tube (Fig. 18-12). Ten mg. of 1:1 sodium carbonate-potassium carbonate mixture are introduced to cover the sample. The crucible is covered and its contents are heated with an oxidizing flame for 2 min.

**Removal of Silica.**—Upon cooling, the lid of the platinum crucible is lifted up, and a few drops of distilled water are run down through the lid into the crucible

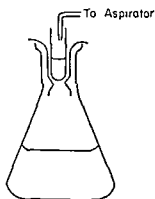


FIG. 18-67. Micro Water Bath.

<sup>56</sup> Benedetti-Pichler, A. A., Llacer, A. J., and Sozzi, J. A., *Anales Farm. Bioquim.*, Buenos Aires, 12, 13, 1941.



to moisten the fusion. One drop of 0.1% methyl red indicator solution is added. Using a dropper with fine capillary tip, 6 *N* hydrochloric acid is carefully introduced along the walls of the crucible, until the solution in the crucible turns red. The solution is then evaporated on the steam bath or metal block. A vent tube, which is connected to the water aspirator, is placed above the surface of the solution (as shown in Fig. 18-67) to hasten evaporation and remove acid fumes. The residue in the crucible is heated at 120°C. for 40 min. Upon cooling, 0.5 ml. of 6 *N* hydrochloric acid is added, and the crucible is heated at 100°C. for 15 min. A few drops of 6 *M* hydrochloric acid are added from time to time to keep the volume constant. Then 0.5 ml. of distilled water is added, and the heating is continued for another 5 min. Calcium and magnesium are brought into solution while silica remains insoluble. A filterstick is now immersed into the liquid and the clear solution is siphoned over and collected in a reaction tube. The platinum crucible and filterstick are rinsed with four 0.2-ml. portions of hot 0.1 *M* hydrochloric acid.

**Removal of Iron, Aluminum, and the Remainder of Silica.**—The solution in the above reaction tube is treated with a few drops of bromine water to convert all iron to the ferric state. The excess of bromine is removed by warming the contents of the reaction tube and aspirating the vapors. A drop of 0.1% methyl red indicator solution is then added. If the red coloration fades immediately, the treatment for the elimination of bromine is repeated. After the removal of bromine, 6 *N* ammonium hydroxide is introduced dropwise until the red color of the solution turns yellow. The contents of the reaction tube are heated at 100°C. for 2 min. to coagulate the precipitate. The liquid containing calcium and magnesium is then transferred, by means of the filterstick, into a clean reaction tube, which was previously weighed with its accompanying filterstick. Four 0.2-ml. portions of 3% ammonium chloride solution are used for rinsing.

**Determination of Calcium.**—To the above reaction tube containing calcium and magnesium ions are added 0.4 ml. of 6 *N* hydrochloric acid and 0.6 ml. of 3% oxalic acid for every 5 mg. of limestone taken. The resulting solution is then treated with 6 *N* ammonium hydroxide, which is introduced drop by drop until a cloudiness is produced. Then the reaction tube is heated in the steam bath or metal block and its contents are swirled from time to time until the turbidity disappears. The solution is diluted, while hot, with distilled water to about 6 ml. after adding one drop of 0.1% methyl red indicator solution, 0.6 *N* ammonium hydroxide is introduced dropwise until the color changes to yellow. The contents of the reaction tube are allowed to cool and stand for 1 hr., or until the precipitate settles in the bottom. The filterstick is immersed in the clear supernatant liquid, which is transferred into another preweighed reaction tube. The precipitate ( $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ) is washed with four 0.75-ml. portions of cold water. The reaction tube and its contents are dried at 100°C. to constant weight.

**Removal of Ammonia and Oxalic Acid.**—The reaction tube containing the filtrate and washings is placed on the steam bath, and the solution is acidified by adding 1 drop of 6 *N* hydrochloric acid, and then evaporated to dryness. The reaction tube is now clamped at an angle of 20° to the horizontal and heated with a small flame to remove the ammonium salts. Oxalic acid sublimes from one part of the reaction tube to the other and cannot be removed by heating alone. The reaction tube is allowed to cool to room temperature and 0.05 ml. of concentrated sulfuric acid is added. By means of a small flame the acid is made to distil up the walls of the beaker and flow over all sublimates of oxalic acid. Finally the whole

reaction tube is heated with the Bunsen burner until all the sulfuric acid is expelled.

**Determination of Magnesium.**—The contents of the reaction tube are allowed to cool, and are redissolved by adding 1.0 ml. of 3 *N* hydrochloric acid for 5 mg. of limestone taken for analysis. The acid is added dropwise just below the rim of the inclined reaction tube, which is rotated so that successive drops of solvent cover the whole wall. The reaction tube is placed on the steam bath for 1 min. If the solution appears turbid, it is filtered into another preweighed reaction tube and the preceding reaction tube is rinsed with four 0.5-ml. portions of distilled water. One drop of 0.1% methyl red indicator solution is added, followed by about 1 mg. of solid ammonium citrate. The reaction tube is placed on the steam bath and its contents are neutralized by adding 0.6 *N*

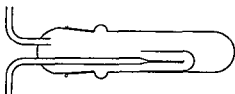


FIG. 18-68. Micro Drying Tube.  
(Courtesy Microchemie.)

ammonia, until the red color changes to yellow. For every 5 mg. of limestone taken for analysis, 0.2 ml. of 1:1 mixture of 6 *N* ammonia and 10% sodium phosphate solution is now added. The contents of the reaction tube are mixed by swirling, and are allowed to stand under cover for 6 hr., or until the originally gelatinous precipitate has been completely converted into the coarsely crystalline  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . The filterstick is introduced and the supernatant liquid is removed. The precipitate is washed with four 1-ml. portions of 0.6 *N* ammonium hydroxide, two 1-ml. portions of ethanol, and 1 ml. of diethyl ether. The reaction tube containing the precipitate and filterstick is now placed in the drying tube<sup>57</sup> shown in Fig. 18-68. A current of dry air is passed through the drying tube, which should not be heated. After 15 min., the reaction tube and its contents are removed from the drying tube and weighed.

### MICRODETERMINATION OF SILICA IN MINERAL SILICATE

**Principle.**—The silicate sample is converted into sodium silicate by fusion with sodium carbonate. The sodium silicate is decomposed by adding hydrochloric acid, and the precipitated silicic acid is dehydrated and rendered insoluble by repeated evaporation with hydrochloric acid followed by baking. Soluble salts are removed by washing and filtration, the ignited crude silica is weighed. The loss observed when the silica is removed by treatment with hydrofluoric acid gives the actual amount of silica present. A small loss of silica occurs during the filtration process owing to slight solubility. For the most accurate results, this silica should be recovered; the method described will, however, give results sufficiently accurate for most purposes.<sup>58</sup>

**Apparatus.** Platinum Crucible.—Crucible, 15-ml. capacity with lid.

**Filterstick.**—See "Microdetermination of the Carbonyl Group by Hydrazone Precipitation," above, p. 410. The filter paper roll should be ashless.

**Procedure.** Preparation of the Sample and Fusion.—A representative sample is prepared as described under "Microdetermination of Calcium and Magnesium in Limestone," above, p. 430. Into the preweighed platinum crucible are added 8 to 10 mg. of the sample, and the crucible is reweighed. Anhydrous sodium carbonate amounting to about 4 times the bulk of the mineral silicate is added. The mixture

<sup>57</sup> Schenck, R. T. E., and Ma, T. S., *Mikrochemie*, 40, 243, 1953.

<sup>58</sup> Briscoe, H. V. A., and Holt, P. F., *Inorganic Micro-Analysis*, Arnold, London, 1950, 128.

is fused for 10 min., the temperature being slowly increased to the maximum during the first 2 or 3 min. Upon cooling, 1 ml. of distilled water is added into the crucible, and the lid is rinsed to wash down particles which may have splashed on it. The uncovered platinum crucible and its contents are placed on a flat glass surface adjacent to a 25-ml. beaker containing concentrated hydrochloric acid. The two crucibles are covered with an inverted crystallizing dish and allowed to stand overnight so that the carbonates and silicates decompose gradually by absorption of hydrochloric acid vapor without risk of splashing. Then the cover is removed and 2 drops of concentrated hydrochloric acid are added into the platinum crucible.

**Baking and Filtration.**—The contents of the platinum crucible are evaporated to dryness on the steam bath (Fig. 18-68), the process being hastened by placing a bent tube connected to the water aspirator above the surface of the liquid. The residue in the crucible is then heated on the metal block at 110°C. for 30 min. The crucible is cooled slightly, and 0.25 ml. of concentrated hydrochloric acid is added, followed by 1 ml. of distilled water. The solution is again evaporated and this process of acidification, evaporation, and baking is repeated twice. Finally 1 ml. of distilled water and 0.25 ml. of concentrated hydrochloric acid are added and the contents of the crucible are warmed for 1 min. on the steam bath. Upon cooling, the filterstick is immersed, the liquid is filtered off, and the precipitate is washed with four 0.5-ml. portions of 6 *N* hydrochloric acid, or until the filtrate becomes colorless, then with 0.5 ml. of ethanol. The filterstick is lifted up and the filter paper roll is extracted with a pair of forceps and dropped into the crucible. After replacing the lid, the crucible and its contents are dried at 100°C. The residue is then ignited at 900°C. to constant weight, which is recorded.

**Treatment with Hydrofluoric Acid.**—Three or 4 drops of hydrochloric acid are added into the above crucible containing silica and other insoluble matters so that the solid is moistened. One drop of concentrated sulfuric acid is added. The crucible lid is replaced, and the crucible is heated with a gentle flame, and finally ignited for 5 min. The crucible and residue are cooled to room temperature and weighed. The difference in weight between the crude silica and the residue after treatment with hydrofluoric acid is the weight of silica present in the sample taken for analysis.

## MICRODETERMINATION OF COPPER AND NICKEL IN GERMAN SILVER

**Principle.**—The copper-nickel alloy is dissolved in the sulfuric-nitric acid mixture. Copper is separated by electrolysis and weighed on the electrode. Nickel remaining in the solution is determined by precipitation and weighing of its dimethylglyoxime chelate.<sup>59</sup>

**Apparatus.** **Apparatus for Electrodeposition.**<sup>60</sup>—A simple micro electrolysis apparatus was described by Benedetti-Pichler (Fig. 18-69). The electrolysis cell is a test tube of 16-mm. diameter and 105-mm. length. The cathode consists of a cylinder of platinum gauze wire of 1-mm. diameter. The end of the wire is bent to a hook so that the cathode may be suspended above the pan of the balance from the hook attached to the stirrup. The gauze cylinder is reinforced at base

<sup>59</sup> Llacer, A. J., Sozzi, J. A., and Benedetti-Pichler, A. A., *Ind. Eng. Chem., Anal. Ed.*, 13, 507, 1941.

<sup>60</sup> Benedetti-Pichler, A. A., *Introduction to the Microtechnique of Inorganic Analysis*, John Wiley and Sons, Inc., New York, 1950, 225.

and top by strong wires, which are welded to the gauze before it is bent into cylindrical shape. Three small glass beads are fused at equal distances from one to another on each of these 2 reinforcing wires. The beads are attached to the base and top of the cylindrical electrode so that they point outward. In this way the

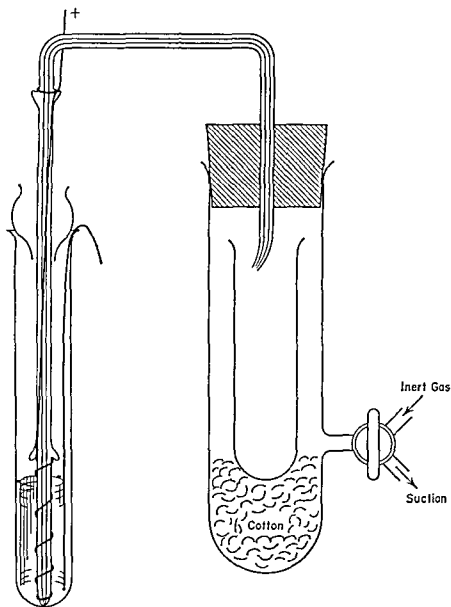


FIG. 18 69. Apparatus for Micro Electrodeposition. (Reprinted with permission from A. A. Benedetti-Pichler, *Introduction to the Microtechnique of Inorganic Analysis*, 1942, John Wiley and Sons, Inc.)

metal deposited on the cathode can easily be prevented from touching the walls of the test tube when the electrode is removed.

The anode consists of a platinum wire 0.5 mm. in diameter, which is wound in the form of a helix around the lower part of the ascending arm of the siphon. The siphon is bent from glass tubing of 2-mm. bore. Two pairs of glass horns keep the anode in its proper position. The stem of the small funnel is wide enough to permit sliding the funnel up and down along the siphon.

The wide suction tube contains a short test tube of 15-ml. capacity for the collection of electrolyte and washings. The 3-way stopcock allows the suction tube to be connected with either a supply of inert gas or with the vacuum line. The electric current is furnished by a storage battery that gives 4 volts. A variable resistance of 50 to 100 ohms is inserted in series with the electrolytic cell, and a voltmeter is hooked up parallel to the cell. Connection with the electrodes is best made by means of small clips which grasp the wires with smooth, polished surfaces (at the points indicated in Fig. 18-69 by plus and minus signs).

**Reaction Tube and Filterstick.**—See Fig. 18-53.

**Procedure. Preparation of the Sample.**—With the empty electrolytic cell held at an inclined position, about 5 ml. of the alloy is accurately weighed into the bottom of the cell by means of the microweighing tube with long handle (Fig. 18-12). To cover the sample, 0.05 ml. of distilled water is introduced. Then 0.02 ml. of concentrated nitric acid is gradually added along the walls of the cell to dissolve the alloy, warming the mixture gently if necessary. This is followed by the cautious addition of 0.01 ml. of concentrated sulfuric acid. When the liberation of nitrogen oxide ceases, the electrolytic cell is washed along its walls with 0.5 ml. of distilled water. The solution is heated on the steam bath for 5 min. while a bent tube connected to the water aspirator is inserted into the electrolytic cell to remove the nitrogen oxide given off by the reaction mixture.

**Electro-deposition of Copper.**—The platinum wire gauze cathode is placed in a short test tube which is half filled with concentrated nitric acid. The test tube is heated on the steam bath for a few minutes. The electrode is removed, rinsed with distilled water, and then dipped successively into 2 large test tubes containing distilled water. It is finally ignited over an oxidizing flame, cooled to room temperature, and accurately weighed.

The platinum cathode is now placed inside the electrolytic cell containing the solution of copper and nickel. One drop of 95% ethanol is added to decrease the stability of the spray,<sup>61</sup> and then sufficient 2 *N* sulfuric acid is introduced to bring the liquid level to near the top of the gauze cylinder. The anode is now inserted into the electrolytic cell and the apparatus is assembled (as shown in Fig. 18-69; the 15-ml. test tube being previously weighed with the accompanying filterstick), while a slow current of nitrogen passes through the suction tube and siphon. The gas flow rate is adjusted to obtain about 1 bubble in 3 sec. This is necessary to prevent the solution from entering the siphon before the complete precipitation of copper. The small funnel is made to rest on the opening of the electrolytic cell, and the space between the stem of the funnel and the siphon is sealed by adding a drop of water. After making the electric connections, the electrolyte is heated to 70°C. in the heating stage. Electrolysis is now started with 2.7 to 3.1 volts across the electrodes. Five min. after the appearance of the copper deposit, the color of the electrolyte will indicate that most of the copper has been precipitated. While the electrolysis is continued, the solution is heated to boiling, and the ring of condensate is allowed to rise close to the opening of the cell. The heating stage is then removed. The funnel and top of the electrolytic cell are rinsed with a few drops of water. The electrolysis is continued for another 10 min. During the second half of this period the electrolyte is cooled by immersing the lower part of the electrolytic cell in a beaker containing cold water. The variable resistance is continuously adjusted so as to prevent the e.m.f. from exceeding 3.1 volts.

<sup>61</sup> Benedetti-Pichler, A. A., *Z. Anal. Chem.*, 62, 321, 1923.

Without interrupting the current, the electrolyte is completely siphoned into the 15 ml. test tube by the application of light suction. The suction is then interrupted, and the electrolytic cell and funnel are rinsed with distilled water until the gauze cylinder of the cathode is again completely immersed. A slow stream of nitrogen is conducted through the wash liquid for 2 min., after which the wash liquid is siphoned into the 15-ml. test tube. This process is repeated twice. Finally the suction is interrupted and the platinum wire gauze is again covered with distilled water. The siphon and anode are removed, and immediately afterwards, the cathode. The latter is quickly placed in a large test tube containing distilled water.

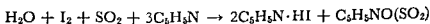
**Weighing of the Cathode with the Copper Deposit.**—The cathode is rinsed by immersing it successively in 2 large test tubes containing distilled water. The excess of water is removed by gently shaking the electrode, which is then dried by heating at a position 300 mm. above a nonluminous Bunsen flame. The electrode is hung on the glass rod to acquire room temperature, and weighed after 5 min. The increase in weight is the amount of copper in the sample taken.

**Determination of Nickel.**—The 15-ml. test tube containing the nickel solution is removed from the suction tube of the electrolytic apparatus and heated on the steam bath to concentrate the solution to about 2 ml. Then are added 0.03 ml. of 6 *N* hydrochloric acid, 1 mg. of ammonium citrate, and 0.03 ml. of 0.1% methyl red indicator solution. The contents of the test tube are mixed by swirling from time to time while 6 *N* ammonium hydroxide is added until the color of the solution changes to yellow. The alkaline solution must remain perfectly clear. It is then diluted to about 4 ml. and heated on the steam bath. Micro drops of saturated ethanolic solution of dimethylglyoxime are introduced by means of a pipet with a fine capillary tip. The contents of the test tube are mixed after the addition of each drop of reagent. The red nickel dimethylglyoximate precipitates and settles rapidly to the bottom of the test tube. Hence, it is easy to recognize when the precipitation is complete. Now 3 more drops of the reagent are added, followed by a volume of distilled water equal to the total amount of the oxime reagent. The test tube with the precipitate is placed on the steam bath for 10 min. It is then allowed to stand for 30 min. before filtration by means of the filterstick, which was previously weighed with the test tube. The test tube and precipitate are washed with four 2-ml. portions of hot water. After the hot wash liquid is completely sucked off, the test tube, filterstick, and nickel dimethylglyoximate are dried at 120°C. for 20 min. and reweighed.

## MICRO TITRIMETRIC INORGANIC ANALYSIS

### MICRODETERMINATION OF WATER BY TITRATION WITH THE KARL FISCHER REAGENT

**Principle.**—The Karl Fischer reagent used in this experiment is a mixture containing iodine, sulfur dioxide, and pyridine in a large amount of anhydrous methyl cellosolve. On reacting with water, the iodine is converted to iodide:



The end point of the titration is determined electrometrically by the "dead stop" method. This is based on the depolarization of the electrodes when an excess of free iodine appears in the solution.

**Apparatus.** Assembly for Micro Titration of Water.—The assembly consists of the Wiberley microburet<sup>62</sup> and a special reaction vessel. As shown in Fig. 18-70, the reaction vessel, *A*, is connected to the microburet by means of the ground-glass joint, and is provided with 3 side arms, *C*, *D*, and *E*. *D* and *E* are for the insertion of the electrodes and the tube with stopcock respectively. The side arm, *C*, is parallel to the base of the flask, and carries a Teflon plunger 60 mm. long. The end of the plunger is cut out to form a trough which holds the microboat, *B*.

**"Dead Stop" Indicator.**—This is commercially available.<sup>63</sup>

**Magnetic Stirrer.**—Any type of magnetic stirrer may be used. The stirring bar should have a diameter less than 3 mm.

**Procedure.** Preparation of the Karl Fischer Reagent.—A stock solution of the Karl Fischer reagent with water equivalent of about 6 mg. per milliliter is prepared as follows: into a 1-liter volumetric flask are added 133 g. of iodine (reagent grade) dissolved in 425 ml. of anhydrous pyridine, followed by 425 ml. of methyl cellosolve; the volumetric flask is closed with the stopper and placed in an ice bath; meanwhile 70 ml. of anhydrous liquid sulfur dioxide are collected, from a tank of pure sulfur dioxide, into a large test tube immersed in the dry ice-acetone cooling mixture; the liquid sulfur dioxide is poured into the volumetric flask in small portions, with constant swirling; the approximate strength of the stock solution is determined by titrating it against sodium tartrate dihydrate. Then a suitable portion of the stock solution is diluted with the appropriate volume of anhydrous methyl cellosolve to obtain a standard solution with the water equivalent of about 2 mg. per milliliter. This solution is transferred into the reservoir, *H*, of the microburet (Fig. 18-70). The funnel, *I*, is closed with a drying tube. After standing overnight, the exact water equivalent of the standard solution is determined by titrating a known sample of sodium tartrate dihydrate against it.

**Determination of Water.**—The apparatus is assembled as shown in Fig. 18-70. If the sample is a solid, it is accurately weighed into a platinum microboat, which is then placed in the plunger and inserted through the side arm, *C*, of the reaction vessel. Two ml. of anhydrous methanol are delivered into the reaction vessel through the side arm, *E*, by momentarily removing the stopcocked tubing. The electrodes are put in place through the side arm, *D*. The plunger is then turned to drop the microboat with the sample into the methanol. The magnetic stirrer

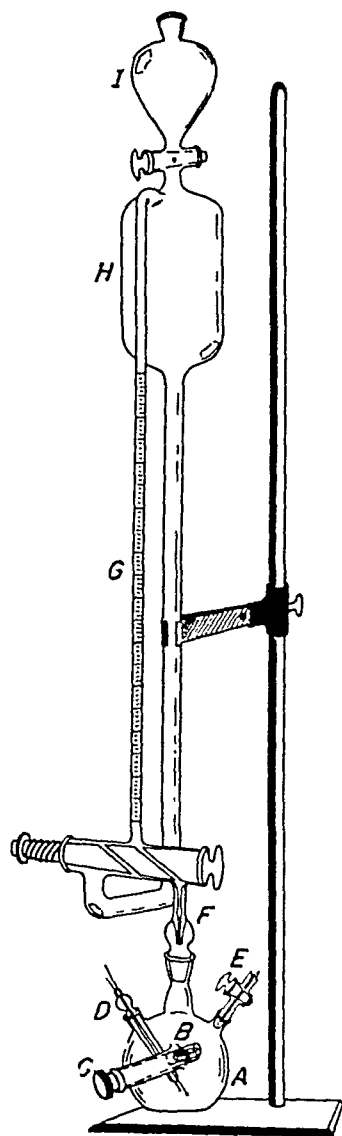


FIG. 18-70. Assembly for Microtitration of Water.

<sup>62</sup> Wiberley, J., *Anal. Chem.*, *Anal. Ed.*, 23, 656, 1951.

<sup>63</sup> Available from Metro Industries, Long Island City, New York.

is switched on, and the Karl Fischer reagent is added from the microburet until the end point is shown by the "dead stop" indicator.

If the sample is a liquid, it is measured by means of a pipet and introduced into the reaction vessel through the side arm, *E*. Enough anhydrous methanol is added to bring the volume of solution in the reaction vessel to 2 ml. A blank should be performed in both cases, using the same procedure and amount of methanol.

### MICRODETERMINATION OF CHLORIDE BY TITRATION WITH MERCURIC NITRATE SOLUTION

**Principle.**—This method is based on the formation of mercuric chloride, which is only very slightly dissociated, and of the colored mercury diphenylcarbazide complex. The chloride ions in nitric acid solution are titrated with standardized solution of mercuric nitrate containing nitric acid. As indicator, 0.1% methanolic solution of diphenylcarbazide is added; the end point is the appearance of violet color.<sup>64</sup> Needless to say, substances that form precipitates or stable complexes with mercury should be absent.

**Apparatus.**—No special apparatus is required.

**Procedure.**—The sample, containing about 3 mg. of chloride, is accurately measured into a 50-ml. Erlenmeyer flask. Solids, which are neutral salts, are dissolved in 5 ml. of 0.01 *N* nitric acid. If the sample is a liquid, it is made up to 5 ml. with 0.01 *N* nitric acid and the pH is adjusted to 2.0 by adding nitric acid or sodium hydroxide solution. Next, 0.5 ml. of the 0.1% diphenylcarbazide in methanol is introduced. The contents of the Erlenmeyer flask are titrated by the standardized 0.01 *N* mercuric chloride solution (in 0.01 *N* nitric acid). The titration is performed against a white background in the daylight, or under a fluorescent lamp. The end point is reached when a permanent bluish violet color appears. In case the operator is not familiar with the color change, the "comparison method" for determining the end point is recommended. This consists of setting up alongside the titration vessel another 50-ml. flask containing the same amount of the indicator solution in 10 ml. of 0.01 *N* nitric acid. A measured amount of the standardized 0.01 *N* mercuric chloride solution is added to the comparison flask to produce the necessary indicator color change. The unknown solution is then titrated until the color is identical in tinge with that of the blank. In the subsequent calculation, the volume of reagent added to the blank is subtracted from the observed titration figure.

### MICRODETERMINATION OF CHLORIDE BY TITRATION WITH SILVER NITRATE SOLUTION

**Principle.**—The chloride ions in a neutral solution are precipitated as silver chloride by titration with 0.01 *N* silver nitrate solution. Dichlorofluorescein is utilized as the adsorption indicator. Acetone is added to the solution to facilitate the observation of the end point.

**Apparatus.**—No special apparatus is required.

**Procedure.**—The accurately measured sample, containing about 3 mg. of chloride, is dissolved in (or diluted to) 5 ml. with distilled water. Three ml. of acetone are added, followed by 2 to 4 drops of 0.02% ethanolic dichlorofluorescein indicator solution. If the solution is neutral, it should have a greenish fluorescence. Otherwise, the pH of the solution is adjusted to 7.0 by adding very dilute nitric acid or

<sup>64</sup> Roberts, I., *Ind. Eng. Chem., Anal. Ed.*, 8, 365, 1936.



sodium hydroxide solution. The neutral solution is now titrated with the standardized 0.01 *N* silver nitrate solution until the color changes from greenish to pink or red. Since the transition point is observed by the color change in a turbid mixture, it is recommended to perform the titration in a darkened room, and to view the titration flask against a darkened background in a beam of transmitted light.

### MICRODETERMINATION OF IRON BY CERIC OXIDIMETRY

**Principle.**—Iron is brought into solution as ferric ions, which are then reduced to the ferrous state. The solution containing Fe(II) is titrated with the standardized 0.01 *N* ceric sulfate solution using Ferroin (*o*-phenanthroline) as the internal indicator. It should be noted that 0.01 *N* ceric sulfate is very unstable, and has to be freshly prepared. It is standardized against a 0.01 *N* ferrous ammonium sulfate solution containing a little sulfuric acid to prevent hydrolysis. Ceric sulfate oxidimetry has an advantage over potassium permanganate, as the former can be used in the presence of hydrochloric acid, which is oxidized by permanganate but not by ceric ions.<sup>65</sup>

**Apparatus.** Silver Reductor.<sup>66</sup>—This is constructed from a glass tube of 7-mm. diameter and 200-mm. length. The top is fitted with a funnel and the bottom joined to a stopcock and capillary tube. The packing is prepared as follows: 10 g. of silver nitrate are dissolved in 0.02 *N* nitric acid in a test tube; a strip of copper foil is immersed into the solution until all the silver is precipitated, and then shaken down to the bottom of the tube; the copper foil is removed and the metallic silver is washed with dilute sulfuric acid until the washing is free from copper.

**Procedure.**—The sample, equivalent to about 5 mg. of iron, is accurately weighed and dissolved in hydrochloric acid. The final solution should have a volume of about 20 ml., and be adjusted to a pH of 0 by means of hydrochloric acid or sodium hydroxide solution. The ferric chloride solution is then poured through the silver reductor at a moderately slow rate and allowed to fall into a 100-ml. Erlenmeyer flask, through which a current of nitrogen is passing to exclude oxygen. The reductor tube is rinsed through with 10 ml. of 1 *N* hydrochloric acid and the rinsing is collected in the Erlenmeyer flask. With nitrogen still passing, 2 to 4 drops of 0.1% Ferroin indicator solution are added, and the contents of the flask are titrated with the 0.01 *N* ceric sulfate solution, freshly prepared from the 0.1 *N* stock solution. The color change at the end point is compared directly with the standard 0.01 *N* ferrous ammonium sulfate solution, which has been just oxidized with the same 0.01 *N* ceric sulfate for the purpose of standardization.

### MICRODETERMINATION OF GOLD BY HYDROQUINONE REDUCTOMETRY

**Principle.**—The gold sample is brought into solution as chlorauric acid. When this is treated with *o*-dianisidine, a color is produced. Titration with the standardized hydroquinone solution reduces the gold from trivalent to the metallic state, with consequent disappearance of the red color.<sup>67</sup>

**Apparatus.**—No special apparatus is required.

<sup>65</sup> Furman, N. H., in Bottger, W., ed., *Newer Methods of Volumetric Chemical Analysis*, D. Van Nostrand Co., Inc., Princeton, 1938.

<sup>66</sup> Van Nieuwenberg, C., and Blumendahl, H., *Microchemie*, 18, 39, 1935.

<sup>67</sup> Pollard, W., *Analyst*, 62, 597, 1937.

**Procedure.**—The ore or alloy, containing about 2 mg. of gold, is treated first with nitric acid. The resulting gold is then dissolved in bromine water and aerated to remove excess of bromine. If the gold is already in solution it is made about *N* acid with hydrochloric acid. Trace amounts of gold in solution are concentrated by coprecipitation with tellurium as follows: a tellurium solution is prepared by dissolving 0.5 g. of tellurium metal in 0.5 ml. of nitric acid and 2 ml. of hydrochloric acid; the solution is evaporated to remove nitric acid, and then 2.5 ml. of concentrated hydrochloric acid are added, and the solution is diluted to 50 ml.; 2 ml. of this solution are added to each liter of solution containing gold, as low as one part in a thousand million; sulfur dioxide gas is passed in until saturation, and the solution is allowed to stand overnight. The tellurium comes down in granular form and carries with it any gold. The precipitate is filtered by suction, and the precipitate and filter paper are transferred to a small crucible, dried, and ignited to remove most of the tellurium. After cooling, the residue in the crucible is treated with 0.3 ml. of concentrated hydrochloric acid and 0.1 ml. of concentrated nitric acid. The crucible is then placed on a water bath for 15 min. to dissolve the precipitated gold. Then a bent tube attached to the water aspirator is placed above the liquid so that air can be drawn over its surface for above 5 min., wherein all nitrogen oxides and free chlorine are removed.

To the solution in the crucible are now added 1 ml. of 5% potassium fluoride buffer solution and 1 ml. of the *o*-dianisidine indicator solution (prepared by dissolving 50 mg. of *o*-dianisidine in 20 ml. of water, adding 0.2 ml. of concentrated hydrochloric acid and diluting to 50 ml. with distilled water). Immediately, the solution is titrated with the standardized hydroquinone solution (1 ml. equivalent to 1 mg. Au; prepared by dissolving 418.6 mg. of pure hydroquinone in 200 ml. of distilled water, adding 10 ml. of concentrated hydrochloric acid and making up to 500 ml.). The end point is the disappearance of the red color.

## MICRODETERMINATION OF MOLECULAR WEIGHTS

### THE CRYOSCOPIC METHOD

**Principle.**—The sample is mixed with a known amount of a suitable solid, in whose melt it dissolves without chemical change. The melting point of the mixture is determined and compared with that of the pure solid solvent. The molecular weight is calculated from the depression of the melting point. Camphor is commonly used as the solvent because it gives a large molal depression value. This method is applicable to the determination of molecular weights of organic compounds only.

The micro cryoscopic method is usually called the micro-Rast method for determining molecular weights. As can be seen from the procedure described below, however, the technique used is different from the semimicro method, which works with decigram quantities of the solid mixture.<sup>68</sup> Less than one mg. of the sample is needed in the micro method, and the result is in general more reliable than that obtained by using many times the amount of sample.

**Apparatus.** Melting Point Tube.—The ordinary melting point capillary should not be used in the micro cryoscopic method for determining molecular weight, because it is not suitable for the introduction of a measured amount of material into the bottom and for sealing the sample without any loss. The melting point

<sup>68</sup> Rast, K., *Berichte*, 55B, 1051, 1922.

tube should have the shape shown in Fig. 18-71. It is made from 10-mm. soft glass tubing, which is thinned out and the tapered section of appropriate dimension is chosen. The narrow end is closed to form a round bottom. A simple way to

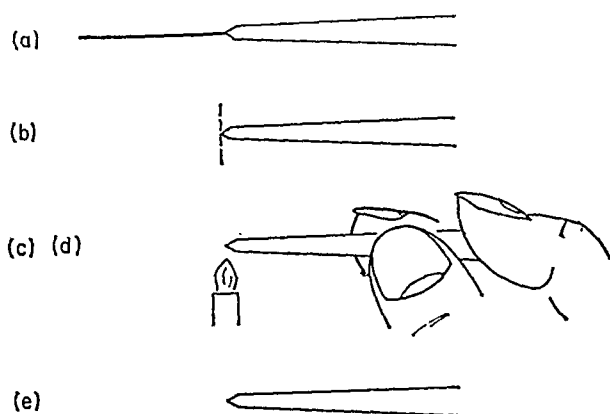


FIG. 18-71. Making the Melting Point Tube for Micro Cryoscopic Method for Molecular Weight Determination.

accomplish this is as follows: (a) the narrow end is heated over a fine flame and drawn out rapidly to a long fine thread; (b) the point near the narrow end of the tapered tube is cut by means of the ampoule cutter; (c) the tapered tube is held by the thumb and middle finger and the wide end is stoppered by means of the index finger; (d) the tip is heated over a fine flame to close the narrow end, which is simultaneously blown out to a round bottom due to the expansion of the trapped air. The finished melting point tube (e) should have a length of about 40 mm., and inside diameter of about 1.5 mm. at the bottom and 4 mm. at the open end. Needless to say, the walls of the melting point tube should be as thin as practicable.

**Capillary and Plunger.**—See Fig. 18-50. Two sets are required, one for solid sample and the other for the solvent. The capillary for semi-solid is shown in Fig. 18-72.

**Procedure. Preparation of the Sample.**—If the sample is a solid, it is finely ground and placed on the micro agate mortar or watch glass. The melting point tube is held in an upright position by inserting it into a tare flask (Fig. 18-3(b), but without lead shots), and the two are weighed together on the microbalance. They are then removed from the microbalance pan and placed in front of the balance case. About 0.5 mg. of the solid sample is pushed into the capillary-and-plunger combination. The latter is wiped with a fine brush, and carefully inserted into the melting point tube until the sample is about 2 mm. from the bottom (Fig. 18-73). If the sample is a semi-solid it is picked up by touching the tip of the micro glass rod (Fig. 18-72) into the sample container and brought inside the melting point tube. In either case, precautions are taken so that no sample touches the upper 30 mm. of the melting point tube. The solid sample is transferred into the melting point tube by being pushed with the plunger; the semi-solid sample is transferred by touching the tip of the micro glass rod to the bottom of the melting point tube.

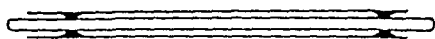


FIG. 18-72. Capillary for Delivering Semi-Solid.

After the proper weight of the sample has been introduced into the melting point tube, about 10 times its weight of finely powdered camphor (or other suitable solvent) is now added by means of the second (and larger) capillary-and-plunger combination. The tare flask, melting point tube, and its contents are again weighed accurately to obtain the exact weight of the solvent added.

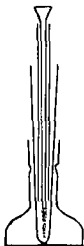


FIG. 18-73 Transferring Solid Sample into the Micro Melting Point Tube.

**Determination of the Melting Point.**—The melting point tube is removed from the tare flask and sealed in the following manner (Fig. 18-74: (a) a micro glass rod is affixed onto the open end of the melting point tube over a fine flame; (b) the melting point tube is heated at a position about 25 mm. from the sample and solvent until the tube is sealed; (c) the section of the melting point tube to the right of the seal is heated until the glass softens to give a solid rod which is drawn out to form a handle, (d).

Another melting point tube is prepared in a similar way containing about 5 mg. of the pure solvent only. Both sealed melting point tubes are now tied to a thermometer by means of fine copper wire (Fig. 18-75). The thermometer and melting point tubes are placed inside the melting point bath such as the apparatus shown in Fig. 18-62. It is important that the entire bulb of the melting point tube be below the surface of the bath liquid. The temperature of the bath is rapidly increased until it is about  $10^{\circ}\text{C}.$  above the melting point of the pure solvent. Then both melting point tubes are allowed to cool inside the bath. When solidification has taken place in both tubes, the process of heating and cooling is repeated. The tube containing the sample is inspected to assure that the fusion is homogeneous, and that there is no sublimate on the walls. If these conditions

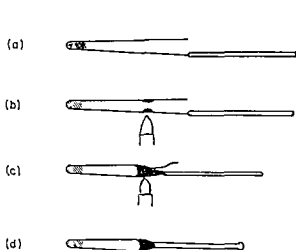


FIG. 18-74. Sealing the Melting Point Tube.

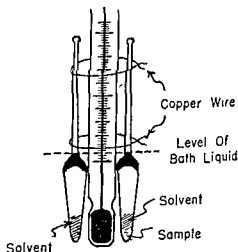


FIG. 18-75. Affixing the Melting Point Tubes for Microdetermination of Molecular Weight.

are not satisfied, the process of melting and resolidification is again repeated. Then the respective melting points of the pure solvent and its admixture are simultaneously determined. The determination is repeated twice. If the melting point of

the admixture is not constant, either the mixing is not yet complete or the sample reacts chemically with the solvent. In the latter case, a different solvent should be employed.

**Calculation of the Molecular Weight.**—The molecular weight of the sample is calculated from the respective weights of the sample and solvent, difference in the melting points of the two tubes, and the molal depression constant of the solvent. The latter value should be determined for each batch of the solvent, using a known compound of high purity.

## THE EBULLIOSCOPIC METHOD

**Principle.**—The ebullioscopic method is dependent on the elevation of the boiling point of a pure solvent due to the presence of a nonvolatile solute. Reduction of the Beckmann technique for determining molecular weight to the milligram scale by the ebullioscopic method has been described by Pregl.<sup>69</sup> It involves the use of a micro-Beckmann thermometer about 180 mm. long and a boiling tube that holds 1.5 ml. of the solution. Difficulty is frequently encountered due to superheating of the liquid and the air current surrounding the apparatus. Rieche<sup>70</sup> has proposed a modification in which the boiling solution is caused to circulate around the mercury bulb of the micro-Beckmann thermometer. Five to 10 ml. of the solution are required, and the observation of the change in boiling point is still difficult. The method using a differential thermometer, as suggested by Menzies and Wright,<sup>71</sup> is suitable for adaptation to microanalysis.

**Apparatus.**—The apparatus proposed by Smith and Milner<sup>72</sup> is shown in Fig.

18-76. The boiling tube, *TFW*, is fitted with the vacuum jacket, *S*, and water condenser, *C*. The boiling bulb, *F*, has a capacity of 3 ml., with the neck, *G*, graduated in 0.1 mm. A tungsten wire, *W*, is sealed in the bulb to prevent bumping; *b*<sub>1</sub> and *b*<sub>2</sub> are 2 enlargements to accommodate the corresponding bulbs *B*<sub>1</sub> and *B*<sub>2</sub> of the differential thermometer. The upper section of the differential

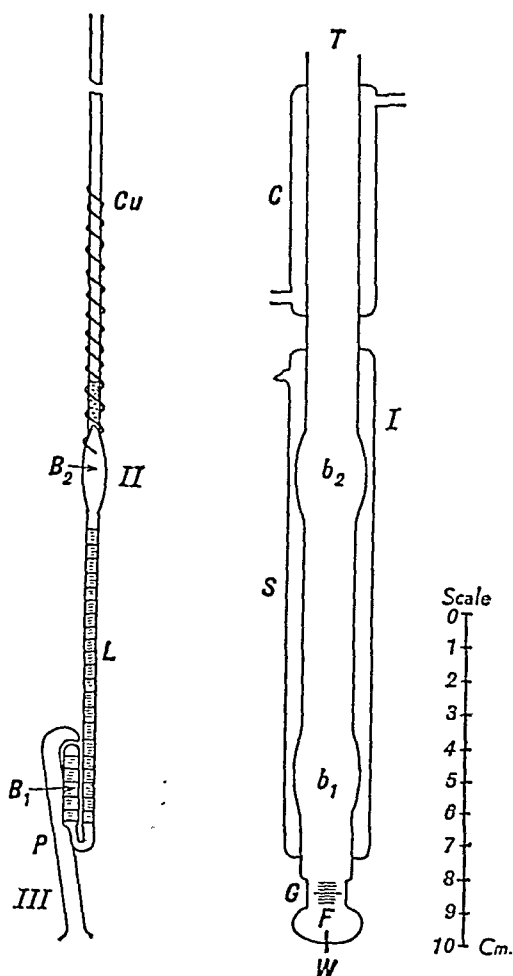


FIG. 18-76. Micro Molecular Weight Apparatus of Smith and Milner.

<sup>69</sup> Roth, H., *Die Quantitative organische Mikroanalyse von Fritz Pregl*, 4th Ed., Springer, Berlin, 1935.

<sup>70</sup> Rieche, A., *Mikrochemie*, 12, 129, 1932.

<sup>71</sup> Menzies, A. W. C., and Wright, S. L., Jr., *J. Am. Chem. Soc.*, 43, 2314, 1921.

<sup>72</sup> Smith, D. F., and Milner, R. T., *Mikrochemie*, 9, 117, 1937.

thermometer is wound with a copper spiral, and the part between the two bulbs  $B_1$  and  $B_2$  is graduated in millimeters.  $P$  is the Cottrell pump.

The apparatus constructed by Balis and co-workers<sup>73</sup> is shown in Fig. 18-77. It can be used for the microdetermination of molecular weight with 1 ml. of the solution.

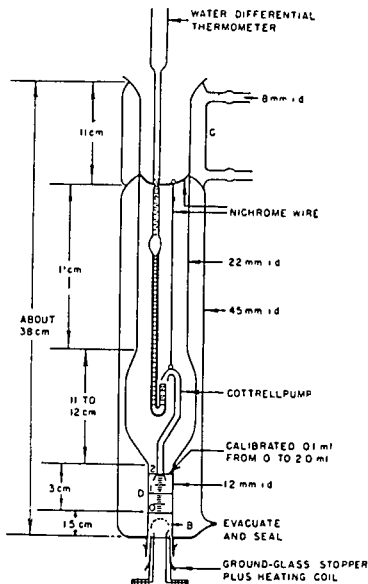


FIG. 18-77. Micro Molecular Weight Apparatus of Balis and Co-workers.

**Procedure.**—The boiling tube, *TFIV* (Fig. 18-76), is clamped in a vertical position, and an asbestos board, with a 5 mm. hole in the center, is placed under the boiling bulb, *F*, so that the tungsten wire, *W*, protrudes through the hole; 3.00 ml. of the pure solvent are delivered into the bulb, *F*. A microburner is placed directly under the tungsten wire, *W*, and is so adjusted that the liquid will reflux gently while water is running through the condenser. A standard thermometer is then inserted into the vapors and the true boiling point of the solvent deter-

<sup>73</sup> Balis, E. W., private communication.

mined to the nearest  $0.1^{\circ}\text{C}$ . The amount of liquid actually present in the boiling bulb, *F*, is then determined by removing the burner, quickly checking the ebullition by touching the bottom of *F* with a beaker of cold water, and immediately reading the volume of the liquid from the graduation, *G*, which has been previously calibrated.

The standard thermometer is now removed and the Cottrell pump lowered into the boiling bulb, *F*, over the tungsten wire, *W*. The differential thermometer is then clamped in such a position that its lower bulb is directly under the opening of the Cottrell pump, but not in contact with it, and that its whole length does not touch any part of the boiling tube, *TFW*. The microburner is replaced and the liquid boiled briskly enough to pump it in an almost continuous stream over the lower bulb of the thermometer. Then at intervals of 1 or 2 min., readings are made (by means of a telescope) on the millimeter scales etched on the thermometer. When the readings have become constant, they are recorded. The sample (10 to 15 mg.), made into the form of a pellet in the pellet press, is accurately weighed and then dropped into the boiling bulb, *F*. Again the liquid level inside the differential thermometer is allowed to reach a constant value, and the reading is recorded. Additional pellets may then be introduced and the corresponding records made. The elevation of the boiling point in degrees C. is obtained from the conversion table,<sup>73</sup> and the molecular weight of the sample is calculated in the usual manner.

### THE ISOTHERMAL DISTILLATION METHOD

**Principle.**—If two solids are dissolved in a common solvent in separate containers and the two solutions are allowed to come to equilibrium with respect to each other, the molar concentration of these solutions will be identical. This is the basis of the isothermal distillation method for determining molecular weight proposed by Signer.<sup>74</sup> Like the ebullioscopic method, this method is applicable to organic and inorganic compounds, and is limited to nonvolatile substances. It should be noted that most inorganic compounds dissociate in solution, while association of molecules is not an unusual phenomenon among organic compounds. Therefore, the result of molecular weight determination should be carefully interpreted.

**Apparatus. The Modified Signer Apparatus.**—The Signer apparatus<sup>74</sup> has been modified by Ma and Jaffe<sup>75</sup> to permit simple and convenient operation. As shown in Fig. 18-78, the apparatus is constructed from 2 graduated pipets, *A* and *B*, sealed to the respective bulbs, *C* and *D*, of 2 ground-glass, capped tubes, which are connected to each other through a cross tube. The latter is provided with a stopcock, *E*. This apparatus is employed when the final volumes of the 2 solutions are measured for the calculation of the molecular weight of the unknown.

**The Apparatus of Morton, Campbell, and Ma.**—This apparatus<sup>76</sup> (Fig. 18-79) is used when the weights of the solvent in the respective vessels are measured in order to obtain the concentrations (by weight) of the final solutions. Since precise measurement of weights is possible by means of the microbalance, this apparatus gives more accurate molecular weights than those obtained by the modified Signer apparatus. As shown in the figure, the solutions are contained in 2 platinum crucibles, of 1.5-ml. capacity, that fit into 2 holes in a metal block placed inside a vacuum

<sup>74</sup> Signer, R., *Ann.*, 478, 246, 1930.

<sup>75</sup> Ma, T. S., and Jaffe, E., unpublished work.

<sup>76</sup> Morton, J. E., Campbell, A. D., and Ma, T. S., *Analyst*, 78, 722, 1953.

desiccator. The desiccator is clamped onto a slowly rocking device. To prevent loss of volatile solvent, the platinum crucibles are weighed inside weighing bottles with tightly fitting ground-glass stoppers.

**Procedure.** Determination by Measuring the Solution Volumes After Equilibrium.—The ground-glass caps of the apparatus (Fig. 18-78) are removed, and stopcock grease is carefully applied so that it will not contaminate the inner walls

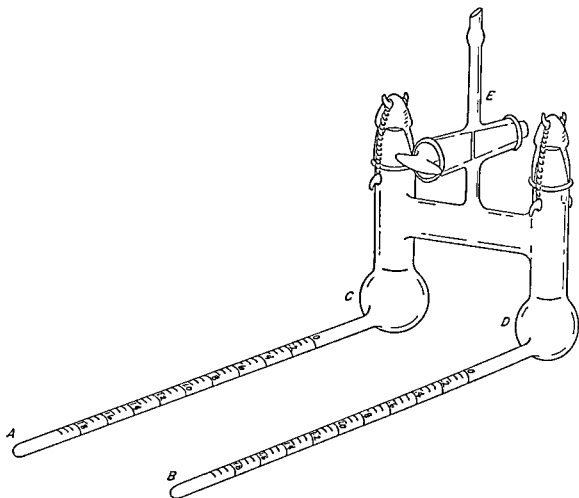


FIG. 18-78. Modified Signer Apparatus for Microdetermination of Molecular Weights.

of the two bulbs, *C* and *D*. Using the microweighing tube (Fig. 18-12), enough of the standard (a known compound of high purity and having solubility behavior similar to that of the unknown) is accurately weighed into the bulb, *C*, to make about 1.5 ml. of approximately 0.1 *M* solution. A suitable amount of the unknown is then accurately weighed into the bulb, *D*, by means of another microweighing tube. The quantity of the sample taken should be such that the final solution will have a concentration of slightly less than 0.1 *M*, and a volume of about 1.5 ml. Three ml. of the solvent are then delivered into each tube by means of a pipet. The glass caps and spring hooks are replaced. The apparatus is slightly tilted so that part of the solvent runs into the respective graduated tubes, *A* and *B*. The stopcock, *E*, is then connected to the vacuum pump to remove the air in the apparatus. When the volume of liquid is reduced to about 1.5 ml. on



each side, the stopcock is closed. The solvent in the graduated tubes, *A* and *B*, is brought back to the 2 bulbs, *C* and *D*, respectively. The apparatus is gently swirled, if the solids have not completely dissolved, to give clear solutions. Then it is placed inside a large aluminum roaster, which is stored in a constant temperature cabinet maintained within  $1^{\circ}\text{C}$ . range day and night. After 24 hr., the apparatus is tilted to transfer the standard solution from *C* to the graduated tube, *A*, and the unknown solution from *D* to *B*. The volumes are recorded and the solutions are then returned to their respective bulbs. This process is repeated

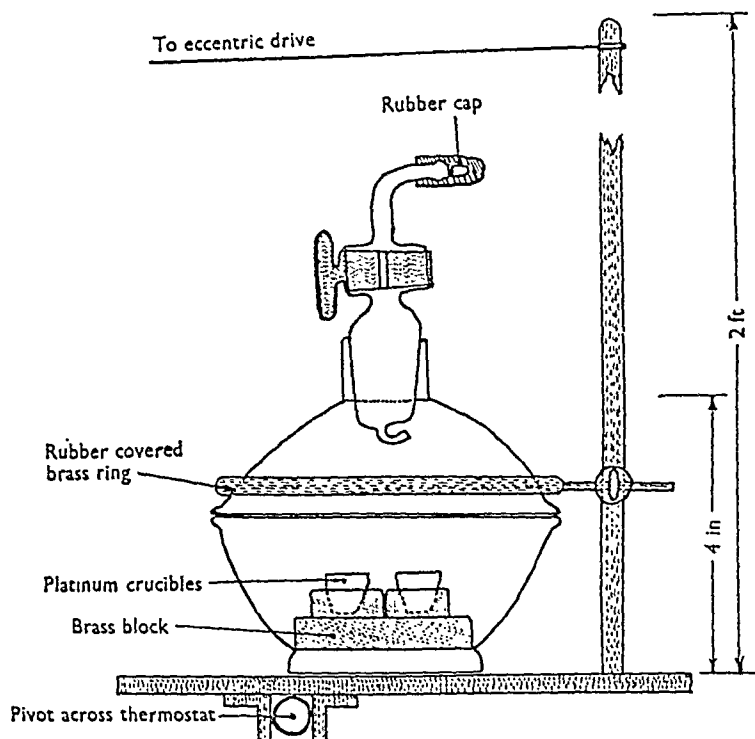


FIG. 18-79. Rocking Desiccator for Micro Molecular Weight Determination.

every 24 hr. until the volumes become constant. From the respective weights of the unknown and the standard, and the volumes of their solutions, the molecular weight of the unknown is then calculated.

**Determination by Measuring the Weights of Solutions After Equilibrium.**—About 5 mg. of the sample are accurately weighed in 1 of the 2 platinum crucibles, and the standard substance is weighed in the other. The crucibles are placed in the holes in the metal block; 0.3 ml. of the solvent is added to each crucible, and 0.5 ml. is poured on the block. The cover of the desiccator is placed in position (see Fig. 18-79) and air is evacuated from the system under controlled conditions so that each crucible still contains 100 to 200 mg. of solvent at the end of the experiment. This is achieved by connecting the desiccator through a large bottle of about 2.5-l. capacity to a water pump. With the connection between the bottle and the desiccator closed, the pressure in the bottle is reduced to 200 mm. of mercury. Then the connection between the bottle and the pump is closed, and that between the bottle and the desiccator is opened to equalize the pressure. The desiccator is disconnected and rocked at 10 strokes per min., through an angle

of 30°, in a thermostat, at 25°C. for 24 hr. At the end of this time, the desiccator is opened and the crucibles are quickly placed inside the respective weighing bottles and weighed. The crucibles are then returned to the desiccator. A few drops of solvent are placed on the metal block, and the apparatus is evacuated as before. After a further 24 hr. of rocking in the thermostat, the crucibles are again weighed.

The solutions are assumed to have attained equilibrium when the ratio of their concentrations (by weight) is constant for 2 concentrations at 24-hr. intervals. The molecular weight of the sample is then calculated from the formula:

$$M_1 = \frac{W_1 S_2 M_2}{W_2 S_1}$$

Where  $M_1$  and  $M_2$  are the molecular weights of the unknown and the standard substance respectively,  $W_1$  and  $W_2$  are the weights of the unknown and standard substance, and  $S_1$  and  $S_2$  are the weights of solvent in the crucible containing the unknown and standard substance, respectively.

### THE THERMO-ELECTRIC METHOD

**Principle.**—This method is dependent on the establishment of, and measurement of, the steady-state temperature difference obtained between drops of a solvent and a solution suspended in the atmosphere of the solvent at a fixed ambient temperature. Two thermistors are used to support the pendant drops and to measure their temperatures. On one thermistor is placed the pure solvent and on the other the solution, while the vessel is saturated with the vapor of the solvent. The solvent temperature remains constant, being subject to equal rates of evaporation and condensation. The solution, however, increases in temperature due to vapor condensation. The temperature difference is proportional to the mole fraction of the solute. It should be noted that the temperature change is extremely small (about 0.03°C.). Therefore, a perfectly matched pair of thermistors is required, and strict temperature control is essential.<sup>77</sup>

**Apparatus.**—The solvent-vapor chamber and thermistor assembly developed by Neumeyer<sup>78</sup> (Fig. 18-80) is composed of a glass vessel, *A*, covered with a Bakelite cap, *B*, which is machined to fit the ground-glass joint. *C* is a stainless steel rod that holds the Teflon thermistor support, *D*. *E* is 5-mm. glass tubing which houses the thermistor, *F*, the latter being affixed by means of cupric oxide-phosphoric acid cement, *G*. *H* is 40-turn platinum wire coil made with 0.3 mm. diameter wire. *I* is 3-mm. thick absorbent paper lining the total depth and about three-fourths of the circumference of the inner wall, and covered on both sides with 1.5 mm. mesh aluminum screen. *J* is a stainless steel crucible to catch the liquid from the thermistor and coil. A pear-shaped solvent-vapor chamber has been proposed by Tomlinson,<sup>79</sup> who claims that this shape produces an effective spherical cell when solvent is introduced into it, thus simplifying theoretical calculations.

The Wheatstone bridge circuit, used with the Neumeyer apparatus (Fig. 18-81), is composed as follows:  $B_1$ , 4.5 volt battery;  $S_1$ , switch,  $R_1$  and  $R_2$ , 100000 ohm variable resistor;  $R_3$ , 1000 ohm variable resistor;  $R_4$ , 20 ohm variable resistor;  $R_5$ , 1000 ohm, 10-turn, wire-wound micropotentiometer;  $TM_1$  and  $TM_2$ , thermistors;  $M_1$ , 0-50 microammeter; and  $M_2$ , null detector.

<sup>77</sup> Simon, W., and Tomlinson, C., *Chimia*, 14, 301, 1960.

<sup>78</sup> Neumeyer, J. J., *Anal. Chim. Acta*, 20, 519, 1959.

<sup>79</sup> Tomlinson, C., *Mikrochim. Acta*, 1961, 457.

**Procedure.**—The solvent-vapor chamber and thermistor assembly are immersed in a thermostat, *L* (Fig. 18-80, at about  $30 \pm 0.01^\circ\text{C}$ . The pure solvent is delivered into the vapor chamber, *A*, so that there is a layer of excess solvent, *K*, about 10 mm. high in the bottom over that required to saturate the absorbent paper, *I*. Both platinum wire coils covering the thermistors are rinsed with 0.1 to 0.2 ml. of solvent. This is accomplished by inserting a long glass dropper through a hole in the Bakelite cap, *B*. The dropper is stored, when not used, in a copper tubing, which is sealed on the bottom and immersed in the thermostat. The micropotenti-

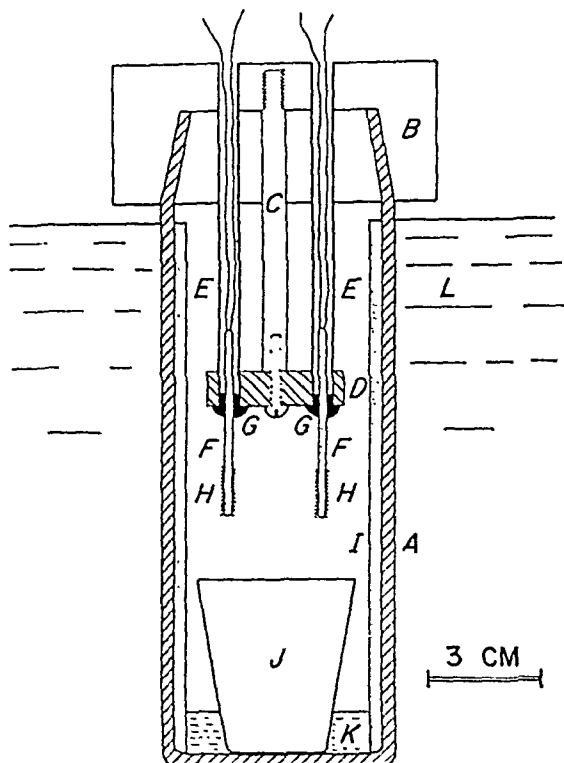


FIG. 18-80. Neumeyer Apparatus for Microdetermination of Molecular Weight.

ometer,  $R_5$  (Fig. 18-81), is set at zero resistance and the switch,  $S_1$ , is turned on. When temperature equilibrium has been established within the vapor chamber, the Wheatstone bridge is balanced using resistors  $R_3$  and  $R_4$ . The solvent in contact with the sensing thermistor,  $TM_1$ , is then replaced by rinsing with 0.1 to 0.2 ml. of solution, which has been previously brought to the temperature of the chamber by immersion of its container in the thermostat. The bridge is again balanced using the micropotentiometer  $R_5$ . About 3 min. are required for the sensing thermistor to reach its maximum temperature. The maximum resistance of the micropotentiometer is recorded. This value is used to calculate the molecular weight of the solute by the formula:

$$M = \frac{W \times M_s(K - \Delta R)}{\Delta R \times W_s}$$

Where  $M$  and  $M_s$  are the molecular weights of the unknown and solvent respec-

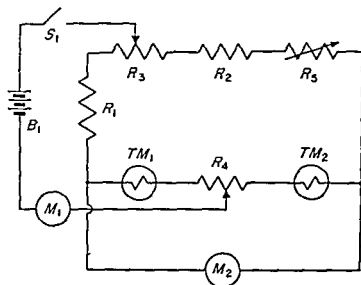


FIG. 18-81. Neumeier Circuit for Microdetermination of Molecular Weight.

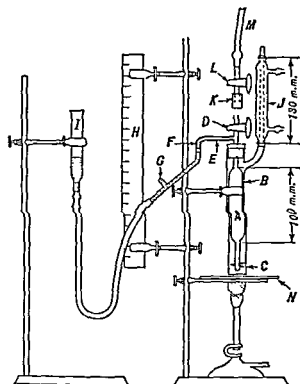


FIG. 18-82. Micro Molecular Weight Apparatus of Bratton and Lochte.

tively,  $W$  and  $W_s$  are the weights of the unknown and solvent in the test solution,  $\Delta R$  is the change in resistance, and  $K$  is a constant for the particular solvent.  $K$  is determined for each solvent by making measurements on pure compounds of known molecular weights.

### THE VAPOR DENSITY METHOD

**Principle.**—A method, which is the micro scale adaptation of the Victor Meyer procedure for determining molecular weight, has been described by Bratton and Lochte.<sup>80</sup> The sample is volatilized under controlled conditions, and the volume of vapor obtained is measured indirectly by observing the change in pressure. This method is applicable only to liquids.

**Apparatus.**—The apparatus<sup>80</sup> (Fig. 18-82) consists of the vaporization chamber,  $A$ , sealed to the manometer,  $FGI$ , and the constant temperature jacket,  $B$ , which is connected to the condenser,  $J$ .  $A$  is supported in  $B$  by a split stopper and the bottom of  $A$  is centered by 3 short glass rods,  $C$ , sealed on  $B$ . The stopcock,  $D$ , of the vaporization chamber,  $A$ , should have a bore of at least 2 mm. so that the capillary containing the sample can pass through it. The side tube,  $E$ , is a capillary tubing, which is joined to a 100-mm. length of 5-mm. tubing. A reference mark for the mercury manometer is etched just below the seal,  $F$ . The vaporization chamber,  $A$ , has 15-mm. outside diameter and 150-mm. length in its wide part; its volume is determined before use by filling with water to the reference mark. The outer jacket,  $B$ , is clamped on a stand, and passes through a hole of the asbestos board,  $N$ .

An apparatus more complicated than that above has been proposed by Sobotka,<sup>81</sup> in which a technique to break the capillary inside the vaporization chamber is described.

**Procedure. Preparation of the Sample.**—A micro-weighing capillary (see "Sample Containers," under "Preparation of Sample for Microanalysis," above, p. 364) is prepared without the air chamber, and with a length of clean iron wire placed in the liquid chamber before making the tip. The outside diameter of the capillary should be smaller than the bore of the stopcock,  $D$ . After about 5 mg. of the sample have been introduced into the capillary, it is sealed to form a hook as shown in Fig. 18-83, and then accurately reweighed.

**Vaporization and Measurement of Pressure.**—A liquid with a boiling point about 20°C. above that of the sample is poured into the outer jacket,  $B$ , to a depth 10 mm. below the end of the vaporization chamber,  $A$ . The manometer is filled with mercury and  $A$  is lifted and tilted to fill trap,  $G$ , which serves to catch any air arising from the manometer. The chamber,  $A$ , is then returned to its original position inside of the jacket,  $B$ . Stopcock  $D$  is closed, and the burner under  $B$  is lighted. The liquid is boiled just vigorously enough so that  $B$  is filled with vapor at all times. Stopcock  $D$  is now opened and the level of the mercury in the right-hand manometer is brought to the reference mark, and  $D$  is again closed. When no change in mercury level has been noted for 5 min., the determination is begun.

Stopcock  $D$  is opened and the capillary containing the sample is inserted. The hook of the capillary rests on the bore of the stopcock while the liquid chamber passes through the stopcock (see Fig. 18-83). The mercury is brought to the

<sup>80</sup> Bratton, A. C., and Lochte, H. L., *Ind. Eng. Chem., Anal. Ed.*, 4, 365, 1932.

<sup>81</sup> Sobotka, M., *Mikrochemie*, 39, 414, 1952.

reference mark, and the level of mercury in *I* is read on the scale, *H*, to 0.2 mm. The stopcock is turned to close the system, simultaneously breaking the capillary, which falls to the bottom of the vaporization chamber, *A*. The leveling bulb, *I*, is gradually raised, and when no further increase in pressure in *A* is noted, the mercury is adjusted to the reference mark and the level in *I* is again read. The difference in the initial and final readings gives the change in pressure in the vaporization chamber *A*. The leveling bulb, *I*, is lowered, and the plug from the broken capillary is removed from the stopcock, *D*. A magnet is then used to guide the capillary out of the vaporization chamber.

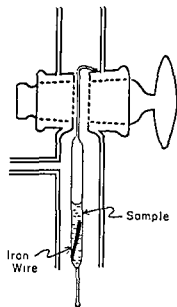


FIG. 18 83. Capillary for Microdetermination of Molecular Weight.

Those compounds that tend to decompose when heated to their boiling point at atmospheric pressure can be vaporized at reduced pressure in the following manner: the capillary containing the sample is inserted in stopcock *D*; stopcock *L* is then connected to *D* by the rubber pressure tubing *K*; *L* is closed, and *M* is connected to a vacuum line; the leveling bulb, *I*, is lowered so that the mercury at *F* falls to a point just above *G*; stopcock *L* is slowly opened and, if necessary, the leveling bulb, *I*, is again lowered; *L* is then closed, and the mercury is brought to the reference mark; if the mercury level remains constant, the level of the mercury is recorded in millimeters, the capillary

tube broken by turning *D*, and the determination completed as previously described.

**Calculation.**—The molecular weight of the sample is calculated by the formula:

$$\text{Mol. wt.} = \frac{22.41 \times 760 \times T \times W}{273 \times V \times \Delta P}$$

Where *T* is the absolute temperature of the vapor bath, *W* is the weight of sample in milligrams, *V* is the volume of the vaporization chamber in milliliters, and  $\Delta P$  is the change in pressure within the vaporization chamber in millimeters of mercury.

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# QUANTITATIVE ORGANIC ANALYSIS

By Sidney Siggia

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This section constitutes a compilation of methods of analysis making possible the quantitative determination of the majority of types of organic chemical materials that will be encountered by an analyst or chemist. All operating details of the procedures are given, and the methods of analysis can be applied directly from this book without referring to the original article or text.

The methods described are limited by the scope of this text. It would be impossible to include all the accepted methods in the allotted space; however, an attempt has been made to cover the common situations. Thus, for example, in the section on carbonyl compounds there is given a general method, a method for aldehydes in the presence of ketones and acetals, and a method for trace carbonyls.

The methods described herein are titrimetric and gravimetric in nature, and the reactions used for the analytical determinations are based on the functional groups on the organic molecule. Methods for measuring some of the less common types of organic compounds, such as imides, sulfoxides, sulfones, amine oxides, and some others are not included.

For more complete coverage of the subject or of the analysis of any particular class of organic compounds, the reader is referred to the following texts:

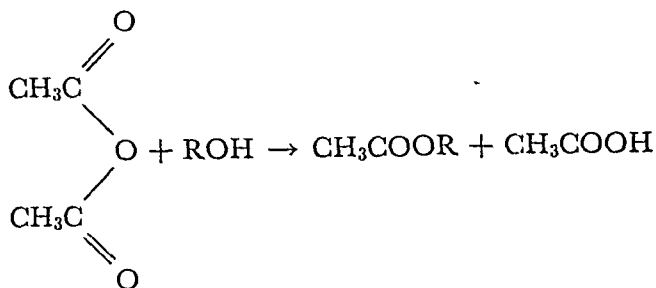
- Mitchell, J., Jr., Koltoff, I. M., Proskauer E. S., Weissberger, A., *Organic Analysis*, Vols. I-III, Interscience Publishers, Inc., New York, 1953-1956.  
Siggia, S., *Quantitative Organic Analysis Via Functional Groups*, 2nd Ed., John Wiley and Sons, Inc., New York, 1954.  
Wild, F., *Estimation of Organic Compounds*, Syndics of the Cambridge University Press, London, 1953.

For texts geared to student instruction, the reader is referred to the following:

- Fritz, J. S., and Hammond, G. S., *Quantitative Organic Analysis*, John Wiley and Sons, Inc., New York, 1957.  
Siggia, S., Stolten, H. J., *An Introduction to Modern Organic Analysis*, Interscience Publishers, Inc., New York, 1956.  
Stone, K. G., *Determination of Organic Compounds*, McGraw-Hill Book Co., Inc., New York, 1956.



## HYDROXY COMPOUNDS

GENERAL METHOD USING ESTERIFICATION WITH  
ACETIC ANHYDRIDEMETHOD 1: UNCATALYZED REAGENT<sup>1</sup>

**Reagents.** Acetylating Reagent.—One volume of ACS grade acetic anhydride and three volumes of reagent pyridine. Reagent should be prepared fresh each day.

*n*-Butanol.—Technical grade.

Mixed Indicator Solution.—One part of 0.1% aqueous cresol red neutralized with sodium hydroxide and three parts of 0.1% thymol blue neutralized with sodium hydroxide.

Standard Alcoholic Sodium Hydroxide (Approximately 0.5 N).—Sodium hydroxide, 0.1 N, can be used for semimicro samples, but the clarity of the end point is poorer than when the 0.5 N reagent is used. Alcoholic sodium hydroxide is best prepared by mixing the required amount of saturated aqueous sodium hydroxide (approximately 18 N) with aldehyde-free ethanol or with c.p. methanol. The alcoholic alkali is standardized against potassium acid phthalate or against standard acid by use of the mixed indicator.

**Procedure.**—A weighed sample containing about 0.010 to 0.016 mole of hydroxyl is introduced into a glass-stoppered iodine flask together with 10.00 ml. of the acetic anhydride-pyridine reagent. The acetylating solution should be accurately measured, a pipet being used. The glass stopper should be well moistened with pyridine and loosely seated. The flask is put on a steam bath for 45 minutes. Then 10 ml. of water is added by way of the well on the top of the flask, and the flask is swirled to bring the water in contact with all the reagent. After 2 minutes, the flask is cooled in ice or under running water, with the stopper partly open to prevent a partial vacuum from forming inside the flask. The sides of the flask and the stopper are rinsed with 10 ml. of *n*-butanol, a few drops of indicator are added, and the contents are titrated with 0.5 N sodium hydroxide. If the sample contains 0.001 mole of hydroxyl, it is advisable to titrate with 0.1 N sodium hydroxide even though the end point may not be as sharp as with the 0.5 N reagent.

Samples which yield highly colored solutions making the indicator useless can be

<sup>1</sup> Method of Ogg, C. L., Porter, W. L., and Willits, C. O., Ind. Eng. Chem., Anal. Ed., 17, 394, 1945, as described by S. Siggia in Quantitative Organic Analysis Via Functional Groups, 2nd Ed., John Wiley and Sons, Inc., New York, pp. 9-12, 1954. Reprinted with permission of the copyright owners.

titrated potentiometrically by use of a potentiometer or pH meter with glass and calomel electrodes.<sup>2</sup>

Any free acid or alkali in the sample should be determined on a separate sample by dissolving the sample in 5 ml. of pyridine and titrating with standard alkali or acid, the mixed indicator being used.

**Calculations.**—Milliliters of NaOH used for blank — milliliters of NaOH used for sample (corrections being applied for any free acid or alkali which may be present) = *A*

$$\frac{A \times N \text{ NaOH} \times \text{OH} \times 100}{\text{Grams sample} \times 1000} = \% \text{ OH}$$

**Discussion.**—If the sample contains considerable water (more than 0.002 mole), additional acetic anhydride should be added to acetylate the alcohol readily. Water does not enter into the calculations, but it does destroy the reagent by hydrolyzing it to acetic acid. If too much reagent is destroyed there would not be sufficient to esterify the alcohol completely.

Primary and secondary amines will interfere in this analysis. In fact, they acetylate so readily that this procedure can be used to determine them quantitatively. Aldehydes of low molecular weight also interfere by reacting with the anhydride.

It is well (keeping the equation in mind) to remember that when all the anhydride is consumed there will still be a titration equal to one-half the blank. If, when unknown samples are analyzed, the titration should be in the vicinity of one-half the blank, it is best to repeat the analysis with a smaller sample to ensure sufficient reagent for the hydroxyl present. Hydroxyl groups on tertiary carbon atoms and hydroxyls of 2,4,6-trisubstituted phenols do react with acetic anhydride but only very slightly. This type of hydroxyl group cannot be determined by this method (there may be exceptions, but these are very few).

#### METHOD 2: REAGENT CATALYZED WITH PERCHLORIC ACID<sup>2</sup>

This catalyzed acetylation has been published fairly recently and does not have the test of time as does Method 1. However, it is known to be more rapid than Method 1 which is uncatalyzed. Also, it is known not to work well in determining hydroxyl groups on easily oxidized compounds such as polyglycol ethers, yielding high, erratic results in these cases. When it can be applied, it is much more economical in time over Method 1.

**Reagents and Solutions.** Acetic Anhydride, 2 *M*, in Ethyl Acetate.—Add 4 g. (2.35 ml) of 72% perchloric acid to 150 ml. of ACS grade ethyl acetate in a clean 250-ml. glass-stoppered flask. Pipet 8 ml. of ACS grade acetic anhydride into the flask and allow it to stand at room temperature for at least 30 minutes. Cool the contents of the flask to 5°C. and add 42 ml. of cold acetic anhydride. Keep the flask at 5°C. for an hour, then allow the reagent to come to room temperature. Some yellow color will develop, but the color and anhydride content of the reagent remain at satisfactory levels for at least two weeks at room temperature.

Acetic Anhydride, 2 *M*, in Pyridine.—Cautiously add 0.8 g. (0.47 ml.) of 72% perchloric acid dropwise to 30 ml. of reagent grade pyridine in a 50-ml. flask. Pipet 10 ml. of acetic anhydride into the flask with magnetic stirring. As this reagent discolors and decreases in anhydride content after a few hours, it should be

<sup>2</sup> Fritz, J. S., and Schenk, G. H., *Anal. Chem.*, 31, 1808, 1959. Copyright 1959 by the American Chemical Society and reprinted with permission of the copyright owner.

prepared fresh daily. For acetylation of sugars at 50°C., use 1.2 g. of *p*-toluenesulfonic acid instead of the perchloric acid.

**Acetic Anhydride, 3 M, in Pyridine.**—Follow the directions above, but use 40 ml. of pyridine, 20 ml. of acetic anhydride, and 0.94 ml. of 72% perchloric acid.

**Sodium Hydroxide, 0.55 M.**—To 185 ml. of saturated aqueous sodium hydroxide (carbonate-free), add 430 ml. of water and 5400 ml. of methyl Cellosolve (Union Carbide Chemicals Company) or absolute methanol. Use only unopened cans of methyl Cellosolve, because solvent which has been opened to the air for some time develops a yellow color in the sodium hydroxide titrant.

**Mixed Indicator.**—Mix 1 part of 0.1% neutralized aqueous cresol red with 3 parts of 0.1% neutralized thymol blue.

**Potassium Acid Phthalate.**—Primary standard grade.

**Alcohol Samples.**—Most liquid samples were fractionally distilled through a 24-in. Podbielniak partial reflux fractional distillation column. Many of the solids were vacuum-sublimed. The estimation purity of the purified samples is in the range 98 to 100%.

**Procedure.**—Weigh accurately a sample containing 3 to 4 millimoles of hydroxyl into a 125-ml. glass-stoppered flask and pipet into it exactly 5 ml. of 2 M acetic anhydride in ethyl acetate or pyridine. Stir the solids or immiscible liquids until they are dissolved. Allow the reaction to proceed for at least 5 minutes at room temperature; some alcohols require a somewhat longer reaction period if pyridine is used as the solvent. Add 1 to 2 ml. of water, shake the mixture, then add 10 ml. of 3 to 1 pyridine-water solution and allow the flask to stand for 5 minutes. Titrate with 0.55 M sodium hydroxide using the mixed indicator, and take the change from yellow to violet as the end point. Titrate dark-colored samples to an apparent pH of 9.8 using glass-calomel electrodes and a pH meter.

Run a reagent blank by pipetting exactly 5 ml. of acetylating reagent into a 125-ml. flask containing 1 to 2 ml. of water solution, allow to stand 5 minutes, and titrate as above. The calculations are as indicated above for the uncatalyzed acetylation.

**NOTE.—Caution.** Dilute solutions of perchloric acid in various organic solvents have been widely used in nonaqueous titrations. There is no hazard under the conditions given in the above procedure. However, solutions acetylated with perchloric acid present should not be heated and the sample and blank solutions should be disposed of promptly after the determination is completed.

Determine sugars which dissolve slowly in the above reagents by heating them 5 to 10 minutes at 50°C. with 5 ml. of a pyridine reagent which is 0.15 M in *p*-toluenesulfonic acid instead of perchloric acid. Moisten the glass stopper with pyridine and seat loosely in the flask. After heating, cool the flask and hydrolyze the anhydride with the 3 to 1 pyridine-water mixture at room temperature. Treat the blank similarly. Dry sugar samples only if analyzed at room temperature.

**Alternate Procedure for Water-Free Samples.**—Use acetic anhydride in ethyl acetate for the acetylation. After the acetylation period, add 10 ml. of a 1.5 M solution of distilled *N*-methylaniline solution of chlorobenzene to the flask instead of the water and water-pyridine solution. After 15 minutes, titrate the excess *N*-methylaniline potentiometrically with 0.2 M perchloric acid in glacial acetic acid. For this titration use a glass indicator electrode and a sleeve-type calomel reference electrode containing lithium chloride in glacial acetic acid as the electrolyte solution. Determine the blank by reacting exactly 5 ml. of the acetic anhydride reagent with 10 ml. of *N*-methylaniline solution as above and titrate

potentiometrically with 0.2 *M* perchloric acid in glacial acetic acid. This procedure is necessary for ethylsulfonylethyl alcohol.

### ESTERIFICATION USING PHTHALIC ANHYDRIDE

Phthalic anhydride has not been used nearly as extensively for the determination of hydroxyl groups as has acetic anhydride. Phthalic anhydride reacts with hydroxyl more slowly than does acetic anhydride. Elving and Warskowsky<sup>3</sup> studied esterification with phthalic anhydride in hot pyridine and confirmed the fact reported by previous workers that this reaction could be used as the basis for determining hydroxyl groups in various alcohols. Aldehydes do not interfere with the alcohol determination when phthalic anhydride is used where it does interfere when acetic anhydride is used.

**Reagent.**—Prepare fresh daily 20 g. of phthalic anhydride in 200 ml. of pyridine.

**Procedure.**—The phthalic anhydride should be acid-free.

Weigh the sample into a 50-ml. volumetric flask. Select a weight of sample that there will be at least a 100% molar excess of phthalic anhydride. Add pyridine to volume and shake thoroughly. Place 25 ml. of phthalic anhydride reagent into a clean, dry, pressure bottle and add 10 ml. of the sample solution. Seal the bottle and place in an air oven at 100°C.; hold at that temperature for 1 hour. At the end of this time remove it from the oven and release the pressure carefully. Add 50 ml. of distilled water, mix, cool under cold tap water, and titrate immediately with sodium hydroxide solution (0.35 *N*) using phenolphthalein indicator. Conduct a blank determination simultaneously and similar in all respects except for addition of the sample.

**Calculation.**—

$$\% \text{ OH} = \frac{(\text{Titration of blank} - \text{titration of sample}) \times N \times 1.701}{\text{Weight of sample}}$$

where *N* = normality of NaOH solution.

### ESTERIFICATION USING PYROMELLITIC DIANHYDRIDE<sup>4</sup>

Acetic anhydride reacts more rapidly than phthalic anhydride, but suffers interference from low molecular weight aldehydes. Phthalic anhydride can be used in the presence of aldehydes. Larger concentrations of phthalic anhydride are necessary for complete reaction. Phthalic anhydride is less volatile than acetic anhydride; therefore, there is less possibility for loss of reagent during heating. Phthalic anhydride can be used to determine alcohols in the presence of phenols. Pyromellitic dianhydride (PMDA) combines the advantages of the two reagents. It can be used in the presence of aldehydes; it is not volatile; it can be used to determine alcohols in the presence of phenols; and its rate of reaction is comparable to that of acetic anhydride. The time involved for analysis is approximately the same as that for the perchloric acid-catalyzed acetic anhydride reaction, although the PMDA method does require a heating period.

<sup>3</sup> Elving, P. J., and Warskowsky, B., *Anal. Chem.*, **19**, 1006, 1947, as described by Mehlenbacher, V. C., *Organic Analysis*, Vol. I, Interscience Publishers, Inc., New York, pp. 35–36, 1953 (later edited by J. Mitchell, Jr., et al.). Reproduced with permission of the copyright owner.

<sup>4</sup> Siggia, S., and Hanna, J. G., *Anal. Chem.* **33**, 900–901, 1961. Copyright 1961 by the American Chemical Society and reprinted in part with permission of the copyright owner.

**Reagents.** Pyromellitic Dianhydride, 0.5 *M*, in Tetrahydrofuran.—The pyromellitic dianhydride can be purchased from E. I. du Pont de Nemours & Company, Inc.

**Procedure.**—A sample containing 0.010 to 0.015 equivalent of alcohol or amine is weighed and placed in a 250-ml. flask. Fifty milliliters of 0.5 *M* pyromellitic dianhydride solution are pipetted into the flask, along with 10 ml. of pyridine. The flask is placed on a steam bath for 2 minutes and then on an electric hot plate for 5 minutes. Most of the tetrahydrofuran will boil off during the heating. Twenty milliliters more of pyridine are added, and the heating continued for 3 minutes. A 20-ml. portion of water is added, and the mixture again heated for 2 minutes to hydrolyze the excess anhydride. The mixture is cooled to room temperature and is titrated with 1 *N* sodium hydroxide to the phenolphthalein end point. A blank is run in the same manner, omitting only the sample.

**Discussion.**—Hydrolyzed pyromellitic dianhydride titrated with standard sodium hydroxide solution showed only one inflection in the plot of volume of titrant vs. pH. The mid point of the maximum slope occurred at pH 9.1 to 9.2 indicating that phenolphthalein is a suitable indicator. Calculated on the basis of alkali consumed up to this point, all four acid groups are neutralized. Tetrahydrofuran was used as the solvent because of the limited solubility of the anhydride in pyridine.

Possible interference from aldehydes was checked by treating 2 to 3 g. each of formaldehyde, acetaldehyde, furfural, and acrolein according to the procedure. No anhydride was consumed in any case. Alcohols to which aldehydes were added were determined. There is no significant interference from the aldehydes. The accuracy and precision by this method are comparable to that obtained by either the acetic anhydride or the phthalic anhydride methods. The recoveries obtained for methanol and ethanol indicate that no special precautions are necessary to prevent loss by volatilization.

Phenols do not react with the pyromellitic dianhydride under the conditions of the procedure. This was proved by the fact that no significant amount of anhydride was consumed when phenols were tried. Tertiary alcohols do react, but not quantitatively; therefore, they cannot be determined by this method.

Any free acidic or basic materials present in the sample should be determined on a separate sample, and the final analysis should be corrected accordingly.

#### DETERMINATION OF HYDROXY COMPOUNDS IN THE PRESENCE OF PRIMARY AND SECONDARY AMINES

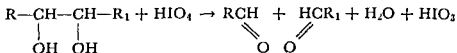
The above esterification methods will quantitatively determine primary and secondary amines along with the hydroxy compound, thus yielding the total value. The amines can be determined by the titration methods shown on p. 488. The esterification value can then be corrected for the amine content of the sample yielding the content of hydroxy compound in the sample.

#### DETERMINATION OF COMPOUNDS WITH ADJACENT HYDROXYL GROUPS (GLYCOLS)<sup>5</sup>

Molecules containing hydroxyl groups attached to adjacent carbon atoms are readily oxidized by periodic acid. The reaction is quite specific and clean cut.

<sup>5</sup> Method of Pohle, W. D., Mehlenbacher, V. C., and Cook, J. H., *Oil & Soap*, 22, 115-119, 1945, as described by Siggia, S., in *Quantitative Organic Analysis Via Functional Groups*, 2nd Ed., John Wiley and Sons, Inc., New York, pp. 16-18, 1954. Reprinted with permission of the copyright owner.

Single hydroxyl groups or hydroxyl groups not attached to contiguous carbons are generally not attacked.



**Reagents.** Sodium Thiosulfate, Standard 0.1 N.

**Oxidizing Reagent.**—To a solution of 5 g. of periodic acid ( $\text{HIO}_4$ ) in 200 ml. of distilled water is added 800 ml. of glacial acetic acid. The solution should be kept in a dark, well-stoppered bottle.

**Potassium Iodide Solution.** 200 g. per liter.

**Starch Indicator Solution, 1%.**

**Procedure.**—A sample containing approximately 0.0005 to 0.001 mole of dihydroxy compound is weighed into a glass-stoppered iodine flask. To the sample is added 100 ml. of oxidizing reagent. A blank is run on the oxidizing agent alone. The solution is allowed to stand for one-half hour at room temperature. (For most compounds one-half hour is sufficient; however, a few samples require 1 hour for complete reaction.) Then 20 ml. of potassium iodide solution is added, and the liberated iodine is titrated with 0.1 N sodium thiosulfate.

**Calculations.**—

$$\text{Milliliters for blank} - \text{milliliters for sample} = A$$

$$\frac{A \times N \text{ thiosulfate} \times \text{mol. wt. compound} \times 100}{\text{Grams sample} \times 2000} = \% \text{ dihydroxy compound}$$

**Discussion.** The procedure as described above was originated to determine various monoglycerides. However, it also works well for other dihydroxyl compounds such as ethylene glycol, mannitol, glycerol (consumes 2 moles of periodic acid per mole glycerol), dextrose, tartaric acid (needs to stand for 1 hour). Expoxide ( $\text{--CH--CH--}$ )



compounds may be determined by this method, but a longer time (one and one-half hours) and an eightfold excess of periodic acid are necessary.

The titration for the sample should be more than 80% of the blank to make sure that enough reagent is present for complete oxidation because the iodate formed in the reaction also liberates iodine from potassium iodide. If all the periodic acid were reacted, the titration would be 75% of the blank. Caution should be taken where the reaction products are formaldehyde or formic acid because these materials are subject to slow, though definite, oxidation at room temperature.

To analyze mixtures of glycerol and dihydroxy compounds this method can be used in combination with the method of Bradford, Pohle, Gunther, and Mehlenbacher.<sup>6</sup> The latter method involves periodic acid oxidation and titration of the formic acid formed by reaction with the glycerol. The method described here will yield both the glycerol and the dihydroxy compound. The difference between the results of both analyses will yield the dihydroxy compound.

In general, periodic acid will not oxidize such compounds as olefins, alcohols, and aldehydes. Some compounds not containing adjacent hydroxyls are attacked. An

<sup>6</sup> Oil and Soap, 19, 189, 1942.

example is 2-butyne-1,4-diol ( $\text{HOCH}_2\text{C}\equiv\text{C}\cdot\text{CH}_2\text{OH}$ ). It oxidizes very slowly, however, but significantly. Most amines are also attacked to some degree.

### DETERMINATION OF ENOLS <sup>7</sup>

Enols are weakly acid compounds that can very often be determined by the acetylation procedure described above, but they can also often be determined quite simply by direct titration in nonaqueous media. Ethylenediamine and dimethylformamide have had quite an extensive tryout, and the procedure is described below.

**Reagents.** Benzene.—Reagent grade.

Dimethylformamide.—Technical grade.

Ethylenediamine.—95 to 100%.

Azo Violet Indicator.—Saturated solution of *p*-nitrobenzeneazoresorcinol in benzene.

*o*-Nitroaniline.—0.15 g. in 100 ml. of benzene.

Thymol Blue.—0.3 g. in 100 ml. of benzene.

Sodium Methoxide, 0.1 to 0.2 *N*.—About 6 g. of sodium are rinsed in methanol. The cleansed sodium is then dissolved in 100 ml. of methanol, and the reaction mixture is cooled if it becomes too vigorous. When all the sodium has reacted, 150 ml. of methanol and 1500 ml. of benzene are added. The solution is protected from carbon dioxide and can be standardized, using benzoic acid as a primary standard. It should be restandardized every few days.

**Procedure.**—Into an Erlenmeyer flask is introduced 20 to 30 ml. of dimethylformamide, and two to three drops of thymol blue or azo violet indicator are added. The solvent is titrated with the sodium methoxide reagent to the blue end point to take care of any free acids in the solvent. The sample is then added and the titration with methoxide is resumed until the blue color is again obtained. Care should be taken to minimize absorption of carbon dioxide by the solution. The basic solvents take up carbon dioxide quite readily. A piece of cardboard over the beaker with a small hole to admit the buret has been found adequate. On potentiometric titration a slight drift will be noted just beyond the end point. This is due to  $\text{CO}_2$  pick-up. For potentiometric titration, the glass and calomel electrodes can be used satisfactorily; usually more solvent has to be used in potentiometric titration if a large amount of titrating solution has to be added. The benzene solvent in the titrant is detrimental to satisfactory operation of the electrodes so that more dimethylformamide has to be present. Antimony-calomel electrodes can also be used.

**Discussion.**—In using ethylenediamine, the same procedure as above is followed, except that the *o*-nitraniline is used as indicator. The end point color change is from yellow to orange-red. The authors of the original paper do not mention having tried potentiometric titration in this medium, and the author of this review has not tried it. However, other investigators <sup>8</sup> have reported the successful use of hydrogen-antimony, hydrogen-calomel, and antimony-antimony electrode systems.

Interferences in the above titration would consist of any acidic material such as acids, phenols, thiols, or acidic amine salts. Active halogen compounds can interfere since they would split out sodium chloride with the titrating reagent. Some

<sup>7</sup> Methods of Fritz, J. S., Anal. Chem., 24, 674-675, 1952.

<sup>8</sup> Moss, Elliott and Hall, Anal. Chem., 20, 784, 1948.

esters interfere, and water is also an interference in the dimethylformamide system, but small amounts do not interfere in ethylenediamine if the indicators are used. Water can be an interference in a potentiometric titration.

### COLORIMETRIC METHOD FOR DETERMINING TRACE QUANTITIES OF HYDROXY COMPOUNDS

Reid and Truelove<sup>9</sup> showed that ceric ammonium nitrate can be used for quantitative determination of alcohols. This method is said to be particularly advantageous for the estimation of small quantities of alcohol in aqueous or water-miscible systems.

**Reagent.**—Dissolve 20 g. of pure ceric ammonium nitrate in 100 ml. of standardized 4 *N* nitric acid. Allow the solution to stand for a day or two until it becomes completely clean and then decant into a clean bottle. Pipet 5.0 ml. of this reagent into a 250-ml. flask and add 50 ml. of dilute  $H_2SO_4$ . Titrate with 0.1 *N* ferrous ammonium sulfate using *o*-phenanthroline as an internal indicator.

**Procedure.**—Add 20 ml. of the reagent to 5.0 ml. of the sample and mix well. At the same time prepare a blank using 20 ml. of the reagent and 5.0 ml. of distilled water. Measure the color exactly 5 minutes after mixing, particularly with the lower alcohols since the colors given by these are less stable than those obtained with higher alcohols. The color obtained is evaluated by comparison with calibration curves prepared from alcohols of known concentration. The originators of the method estimated the color in a 1-cm. Skepper cell using a Hilger OG1 olive-green filter.

**Discussion.**—Complete information as to interfering substances is not available; however, it is assumed that other compounds containing hydroxy groups, sulfates, and certain oxidizing and reducing substances may lead to incorrect results. The method has been applied to the following compounds: methyl alcohol, ethyl alcohol, isopropyl alcohol, *n*-butyl alcohol, *sec*-butyl alcohol, *tert*-butyl alcohol, monoethylene glycol, diethylene glycol, and triethylene glycol.

## CARBONYL COMPOUNDS

### GENERAL METHOD FOR DETERMINING CARBONYL COMPOUNDS USING THE OXIMATION REACTION<sup>10</sup>

**Reagents.** 2-Dimethylaminoethanol, 0.25 *M*.—Dissolve approximately 22.5 g. of freshly distilled 2-dimethylaminoethanol (Eastman Chemical Products, Inc., white label or equivalent) in 2-propanol to make 1 liter of solution.

Hydroxylammonium Chloride, 0.4 *M*.—Dissolve 27.8 g. of the pure salt in 300 ml. of absolute methanol and dilute to 1 liter with 2-propanol.

2-Propanol.—Reagent grade, absolute.

Martius Yellow.—Dissolve 0.0667 g. of Martius yellow (Harleco, Hartman-Teddon Company) and 0.004 g. of methyl violet in ethanol and dilute to 50 ml. with ethanol.

<sup>9</sup> Method of Reid, V. W., and Truelove, R. K., *Analyst*, **77**, 325, 1952 as described by Mehlenbacher, V. C., *Organic Analysis*, Vol. I, Interscience Publishers, Inc., New York, p. 48, 1953 (edited by J. Mitchell, Jr., et al.). Reprinted with permission of the copyright owner.

<sup>10</sup> Method of Fritz, J. S., Yamamura, S. S., and Bradford, E. C., *Anal. Chem.*, **31**, 260, 1959. Copyright 1959 by the American Chemical Society and reprinted with permission of the copyright owner.



**Methyl Cellosolve.**—Merck & Company, Inc., reagent grade or Union Carbide Chemicals Company.

**Perchloric Acid, 0.2 M.**—Pipet 17.0 ml. of 70% perchloric acid and dilute to 1 liter and methyl Cellosolve. Standardize by titration of tris(hydroxymethyl)amino-methane.

**Tris(hydroxymethyl)aminomethane.**—Primary standard grade.

**Procedure.**—Weigh the sample containing 1.5 to 2.5 millimoles of reactive carbonyl into a 150-ml. glass-stoppered flask. Add exactly 20 ml. of 0.25 M 2-dimethylaminoethanol, then add exactly 25 ml. of 0.4 M hydroxylammonium chloride. Stopper the flask, swirl gently to mix, and let stand the required length of time. Ten minutes at room temperature is sufficient for most aldehydes and simple aliphatic ketones. Check doubtful compounds, using a longer reaction time. Aryl ketones, hindered aliphatic compounds, and dicarbonyl compounds require an oximation period of 45 minutes or longer at 70°C. Add five drops of Martius yellow indicator and titrate with 0.2 M perchloric acid. Take the change from yellow to colorless or blue-gray as the end point.

Determine the blank by titrating a similar mixture of 2-dimethylaminoethanol and hydroxylammonium chloride that has stood for the same period of time as the sample. Use the difference between the blank,  $V_b$ , and the sample titration,  $V_s$ , to calculate the percentage of the carbonyl compound in the sample.

$$\% \text{ Carbonyl compound} = \frac{(V_b - V_s)(\text{conc. HClO}_4)(\text{mol. wt.})}{10(\text{sample wt., g.})}$$

## GENERAL METHOD FOR DETERMINING ALDEHYDES BY BISULFITE ADDITION <sup>11</sup>

**Reagents.** Sodium Sulfite, 1 M.

Sodium Hydroxide, Standard 1 N.

Sulfuric Acid, Standard 1 N.

**Procedure.**—To 250 ml. of 1 M sodium sulfite in a 500-ml. glass-stoppered Erlenmeyer flask is added 50 ml of 1 N sulfuric acid. The flask is swirled as the acid is added, to prevent the loss of sulfur dioxide caused by localized overneutralization of the sodium sulfite. To this solution is added, sealed in a glass ampoule, a sample containing 0.02 to 0.04 mole aldehyde. The flask is then stoppered, the stopper being greased for low-boiling aldehydes to prevent any loss. It is then vigorously shaken to break the ampoule containing the sample. Some glass beads included in the flask with the ampoule will cause the ampoule to break more easily. The flask is then shaken for 2 to 3 minutes (5 minutes for the more insoluble aldehydes) to ensure complete reaction. The contents are then quantitatively transferred to a beaker. Electrodes from a pH meter are inserted in the solution, and the solution is stirred. The pH of the solution is noted as standard 1 N alkali is added to titrate the excess acid.

For accurate results, the pH reading vs. milliliters of alkali added are noted and plotted. The end point is determined from the plot. A more rapid method of determining the end point, though slightly less precise, is to add alkali until a pH

<sup>11</sup> Method of Siggia, S., and Maxcy, W., Ind. & Eng. Chem., Anal. Ed., 19, 1023, 1947, as described by Siggia, S., in Quantitative Organic Analysis Via Functional Groups, 2nd Ed., John Wiley and Sons, Inc., New York, pp. 24-27, 1954. Reprinted with permission of the copyright owners.

is obtained corresponding to the pH at the end point for the particular aldehyde. This end point pH must be predetermined for the aldehydes.

Sodium sulfite contains a small amount of free alkali as an impurity so that 250 ml. of the solution consumes some acid. The blank is very small but not negligible; it amounts to about 0.4 to 0.5 ml. of 1 *N* acid per 250 ml. of sulfite solution. On each carboy of sodium sulfite solution prepared, the free alkali should be accounted for, or the aldehyde results will be slightly high. Rather than use a blank on the sulfite solution, it was found more satisfactory to add sufficient 1 *M* sodium bisulfite to the sodium sulfite to neutralize the free alkali and bring the pH of the sulfite to 9.1. This procedure eliminates the need of a blank and may be done only once to each carboy of solution.

#### Calculations.—

*A* = Calculated amount of NaOH standard solution needed to titrate the 50 ml. of standard acid used — the milliliters of standard NaOH used to titrate the sample

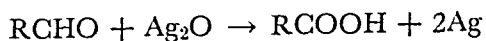
$$\frac{A \times N \text{ NaOH} \times \text{mol. wt. compound} \times 100}{\text{Grams sample} \times 1000} = \% \text{ compound}$$

**Discussion.**—In the case of most of the aldehydes used, the end point was sharp enough so that the rapid method of just titrating to the pH of the end point could cause an error in end point determination of only  $\pm 0.2$  to 0.3 ml. This error is not very significant and can be nullified by using a rather large sample of about 0.04 mole of aldehyde, which consumes 40 ml. of 1 *N* acid. It can readily be seen that a plot of pH vs. milliliters of sodium hydroxide is not necessary once the pH at the end point of the particular aldehyde is determined. The reproducibility of the procedure is  $\pm 0.2\%$  if the entire curve is plotted and  $\pm 0.4\%$  if the rapid method is used.

Acidic or basic impurities in the sample should be determined separately before the aldehyde procedure is applied, and the titration for the aldehyde should be corrected for the presence of these impurities.

Acetals will not interfere in the procedure. These compounds hydrolyze in strong acid solution to yield acetaldehyde. However, the pH of the sodium sulfite-sulfuric acid solution, in proportions described in the procedure, is about 6.8, and there is no noticeable hydrolysis of the acetals at this pH. Also, the aldehyde in the sample consumes the bisulfite so rapidly that the pH of the solution is raised to about 7.5 as soon as the sample comes in contact with the sodium sulfite-sulfuric acid solution, further lessening any possibility of hydrolysis.

Ketones, in general, will not interfere in this determination of aldehydes if they are not present in excess of about 10% per mole of the total carbonyl content. Ketones affect the slope of the titration curve and the pH at the end point but do not affect the final result. Too high a ketone content causes the inflection point in the curve to disappear. This behavior is caused by the loose binding of bisulfite by ketones.

OXIDATIVE METHODS FOR ALDEHYDES ALONE OR IN THE PRESENCE OF KETONES AND ACETALS<sup>12</sup>

**Apparatus and Materials.** *Shaking Machine.*—One of suitable construction to accommodate two or more 100-ml., or 250-ml. volumetric flasks.

*Water Bath.*—Maintained at  $60^\circ \pm 2^\circ\text{C}$ .

*Ethyl Alcohol, Absolute.*—If appreciable carbonyl compounds or other reactive impurities are present, purify the solvent by distilling over excess solid silver oxide.

**Procedure.**—Pipet 25.0 ml. of 0.1 *N* silver nitrate solution into a 100-ml. volumetric flask. Add a quantity of sample containing approximately 0.5 millimole of aldehyde. If the sample is volatile, or the carbonyl content is high, weigh the required amount in a glass ampoule. If the sample is not volatile from water or alcohol, the sample containing 5 millimoles of aldehyde may be dissolved in 100 ml. of water or alcohol and a 10-ml. aliquot of the solution may be taken for analysis. Add 5 ml. of 0.5 *N* sodium hydroxide solution and shake the mixture on a shaking machine for 15 minutes. At the end of this time, add 2 ml. of 0.5 *N* sodium hydroxide solution and continue the shaking for 10 minutes. Add 10 ml. of 6 *N* sodium hydroxide solution and repeat the shaking for the same period of time. Acidify the reaction mixture with 5 ml. of 18 *N* sulfuric acid solution. After allowing the mixture to cool to room temperature, dilute to the mark with distilled water. Filter the mixture through a dry No. 41 Whatman filter paper into a 400-ml. beaker. Pipet 50.0 ml. of the filtrate into a 500-ml. glass-stoppered Erlenmeyer flask and add 4 ml. of ferric alum indicator. Titrate with 0.05 *N* thiocyanate solution until the end point is approached, as indicated by a more slowly fading red color. Stopper the flask, shake vigorously for 20 to 30 seconds, and continue the titration until one drop produces a reddish coloration which does not fade upon swirling or vigorous shaking. Carry out a blank determination by following the procedure as described but omitting the sample.

**Calculation.**—

$$\frac{(A - B) \times N_{\text{ens.}} \times \text{mol. wt. aldehyde} \times 100}{\text{Gram sample} \times 2000} = \% \text{ aldehyde}$$

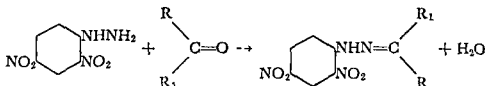
in which *A* = blank titration, and *B* = sample titration.

GRAVIMETRIC METHOD FOR DETERMINING SMALL QUANTITIES OF CARBONYL MATERIALS<sup>13</sup>

This procedure employs the standard identification reaction for carbonyl compounds. This reaction is essentially quantitative for many aldehydes and ketones, making the procedure quite generally applicable.

<sup>12</sup> Siegel, H., and Weiss, F. T., *Anal. Chem.*, 26, 917, 1954. Copyright 1954 by the American Chemical Society and reprinted with permission of the copyright owners.

<sup>13</sup> Method of Iddles, H. A., and Jackson, C. E., *Ind. & Eng. Chem., Anal. Ed.*, 6, 454–456, 1934, as described by Siggia, S., in *Quantitative Organic Analysis Via Functional Groups*, 2nd Ed., John Wiley and Sons, Inc., New York, pp. 31–32, 1954. Reprinted with permission of the copyright owners.



where R and R<sub>1</sub> could be a hydrogen atom.

The reaction is also very specific; interferences consist mainly of materials that will oxidize the hydrazine to form tars, which are weighed with the hydrazones. This procedure is also applicable to the determination of acetals, ketals, and vinyl ethers. Since the hydrazine is in acid solution, it will hydrolyze the above-mentioned compounds to the corresponding aldehyde or ketone, which will then react with the reagent.

The procedure described below is designed for water-soluble samples only. However, since such a small amount of carbonyl compound is necessary ( $40 \times 10^{-5}$  mole), one can usually dissolve enough sample in water to yield enough carboxyl compound for analysis.

**Reagents.** 2,4-Dinitrophenylhydrazine.—A saturated solution at 0°C. in 2 N aqueous hydrochloric acid solution. This solution contains about 4 mg. hydrazine per ml.

**Hydrochloric Acid Solution, 2 N.**

**Procedure.**—In a glass-stoppered flask is placed 50 ml. of reagent. To this is added the sample, which should contain approximately  $40 \times 10^{-5}$  mole of aldehyde. The mixture is allowed to stand in an ice bath for 1 hour. In the case of the volatile carbonyl compounds such as acetaldehyde or acetone, it is advisable to shake the flask vigorously from time to time to ensure the reaction of any carbonyl material which may be in the atmosphere above the reagent. After the period of standing, the precipitate is filtered off into a tared Gooch crucible or into a tared sintered glass funnel. The precipitate is washed with 2 N hydrochloric acid, then with water, and is dried in a vacuum desiccator over sulfuric acid. The precipitates can usually also be dried in an oven at 100°C.

**Calculations.**—

$$\frac{\text{wt. hydrazone}}{\text{wt. sample}} \times \text{gravimetric factor} \times 100 = \% \text{ carbonyl compound}$$

## COLORIMETRIC METHODS FOR TRACES OF CARBONYL MATERIALS

### COLORIMETRIC 2,4-DINITROPHENYLHYDRAZONE PROCEDURE<sup>14</sup>

**Procedure.**—To 1 ml. of sample solution, adjusted to a concentration of  $10^{-4}$  to  $10^{-6}$  M, are added 1.0 ml. of 2,4-dinitrophenylhydrazine reagent (saturated carbonyl-free methanol solution) plus one drop of concentrated hydrochloric acid. The mixture is heated on a water bath at 50° for 30 minutes or at 100° for 5 minutes. After cooling, 5.0 ml. of 10% potassium hydroxide in 80% aqueous methanol is added. The nearly black solution clears almost immediately to the characteristic wine-red color. The absorbancy is measured at 480 mμ. A blank

<sup>14</sup> Lappin, G. R., and Clark, L. C., *Anal. Chem.*, **23**, 541-542, 1951.

determination is made simultaneously using 1.0 ml. of carbonyl-free methanol in place of the sample.

The concentration of carbonyl compounds in the sample is determined either by calculation or by reference to a standard curve.

### *COLORIMETRIC DETERMINATION FOR ALDEHYDES USING SCHIFF REAGENT*<sup>15</sup>

Schiff reagent, prepared from rosaniline hydrochloride (basic fuchsin) and sulfur dioxide, was used in one of the earliest tests for aldehydes.

Careful control of the ratio of sulfur dioxide to fuchsin was necessary for the preparation of the most sensitive reagent. For example, Tobie<sup>16</sup> dissolved 0.5 g. of basic fuchsin in 500 ml. of water and added 1.0 g. of sulfur dioxide. After allowing the solution to stand overnight, most of the red color had disappeared. The reagent was diluted to 1 liter with water and 1.0 g. of decolorizing carbon was added to remove the residual color. Tobie found that this method of preparation gave a reagent of sufficient sensitivity for use in the estimation of free aldehyde groups in aldoses. Storage of the reagent in a hydrogen atmosphere is recommended as an aid in stabilizing the reagent.<sup>17</sup>

The use of sulfites probably presents a more convenient method than direct sulfur dioxide addition for the preparation of Schiff reagent. Feulgen and Grünberg<sup>18</sup> and Hoffpauir and his co-workers<sup>19</sup> dissolved 1.0 g. of fuchsin in 100 ml. of 1 *N* hydrochloric acid, added 5 g. of sodium bisulfite, and diluted the solution to 1 liter. Alexander and his co-workers<sup>20</sup> prepared the reagent in a few minutes by adding 0.5 g. of active sodium hydrosulfite to 100 ml. of 0.5% basic fuchsin. About 0.2 g. of activated carbon was added and the mixture was filtered. The resulting solution was light amber in color.

Varying shades of red to blue-violet are given by reaction of aldehydes with Schiff reagent. The intensity of the color is function of the concentration of aldehyde in the sample.

## DETERMINATION OF ACETALS

### *OXIMATION*

Acetals can be determined by hydrolysis and oximation, both of which are effected by treatment with an 0.5 *N* aqueous solution of  $\text{NH}_2\text{OH}\cdot\text{HCl}$ . Methyl alcohol can be used to help dissolve the sample; however, the final solution should contain more than 10 to 25% water for the hydrolysis to be efficient. The acidity of the  $\text{NH}_2\text{OH}\cdot\text{HCl}$  is generally enough to cause hydrolysis, especially since the solution becomes more acidic as oximation proceeds.

Acid can be added to hasten hydrolysis, but its amount must be deducted in the final calculation.

The reaction mixture can be allowed to stand at room temperature for one-half

<sup>15</sup> Mitchell, J., Jr., *Organic Analysis*, Vol. I, p. 284, Interscience Publishers, Inc., New York, 1953.

<sup>16</sup> Tobie, W. C., *Ind. Eng. Chem., Anal. Ed.*, **14**, 405-406, 1942.

<sup>17</sup> Fischbeck, K., and Neundeubel, L., *Z. anal. Chem.*, **104**, 81-88, 1936.

<sup>18</sup> Feulgen, R., and Grünberg, H., *Z. physiol. Chem.*, **257**, 161-172, 1939.

<sup>19</sup> Hoffpauir, C. L., et al., *Ind. Eng. Chem., Anal. Ed.*, **15**, 605, 1943.

<sup>20</sup> Alexander, J., et al., *Science*, **111**, 13, 1950.

to 1 hour in the case of the simple acetals. Refluxing can be used to accelerate the reaction in more stubborn cases.

The final reaction mixture is titrated potentiometrically with 0.5 or 0.1 *N* NaOH to the inflection point.

The calculation is based on the following equation:

$$\% \text{ Acetal} = \frac{\text{Ml. NaOH} \times N \text{ NaOH} \times \text{Mol. Wt.} \times 100}{\text{Grams sample} \times 1000}$$

Free aldehyde interferes and corrections for it should be made, applying the bisulfite method shown on p. 463.

Formals generally are too resistant to hydrolysis to permit analysis by this method. However, a few cases can be determined after 2 hours of reflux.

#### HYDRAZONE FORMATION

The analysis using 2,4-dinitrophenylhydrazine given on p. 466 can be applied to acetals. The method can be used on formals as well, since the hydrolytic conditions are more intense than those used above.

The solubility of the sample and of the precipitate are the limiting factors in the application of this method.

Traces of acetals can be determined using the colorimetric method given on p. 466.

### CARBOXYLIC ACIDS

#### GENERAL METHOD USING TITRATION WITH BASES<sup>21</sup>

Carboxylic acids are most simply determined by titration with standard alkali. An aqueous system is usually adequate if the sample dissolves in water. If the sample is insoluble in water, it may dissolve in excess aqueous caustic, and the excess caustic is titrated. A potentiometric titration is advisable when one is working with acids of unknown strength; an appropriate indicator can be chosen when the pH at the titration break has been determined.

For samples which are water insoluble or samples which give poor titration curves in an aqueous system, a nonaqueous system can be used. Much sharper breaks are obtained for weak acids in acetone, dimethylformamide, methanol-benzene, and ethylene glycol-isopropanol than are obtained in water. Out of these four, at least one solvent can be found that will dissolve stubborn samples.

In the acetone solvent, the sample can be titrated with 0.1 *N* alcoholic (methanol) caustic. The ordinary glass and calomel electrodes can be used in potentiometric titrations in this solvent.

In dimethylformamide,<sup>22</sup> the sample can be titrated with 0.1 to 0.2 *N* sodium methylate in benzene-methanol. (About 5 g. of sodium are cleaned with methanol and then dissolved in 100 ml. of absolute methanol. Cooling in ice water may be necessary at times to slow down the reaction. When all the sodium has reacted, 150 ml. of methanol and 1500 ml. of benzene are added.) Thymol blue in a 0.3%

<sup>21</sup> Siggrå, S., *Quantitative Organic Analysis Via Functional Groups*, 2nd Ed., John Wiley and Sons, Inc., New York, pp. 41-42, 1954. Reprinted with permission of the copyright owners.

<sup>22</sup> Fritz, J. S., *Acid-Base Titrations in Nonaqueous Solvents*, The G. Frederick Smith Co., Columbus, Ohio, pp. 28-29, 1952.

solution in methanol can often be employed as indicator. The glass and calomel electrodes can be used in this solvent as can the antimony-calomel electrodes.

Benzene-methanol<sup>23</sup> is a good solvent for titrating acids. The titrant is the same as that used in dimethylformamide. The authors claim that an antimony vs. a calomel electrode should be used and that a little lithium chloride should be added to decrease the resistance in the solutions. However, the author of this section has been able to use the glass and calomel electrode satisfactorily without electrolyte. There may be a difference in behavior of the electrodes depending on the materials being determined, so it is best to keep both electrode systems in mind should one fail to operate in the particular analysis being made.

A 1:1 ethylene glycol-isopropanol system has been used<sup>24</sup> for titrating weak acids. In titrating acids, alcoholic sodium hydroxide is used as titrant. The breaks obtained in this solvent are usually not as intense as those obtained in the aforementioned organic solvents. However, the breaks are still quite good, and, since this mixture is an excellent solvent, it can be applied to samples which may be difficultly soluble in the above solvents. The glass and calomel electrodes can be used in this solvent mixture.

## CARBOXYLIC ACID SALTS

### GENERAL METHOD USING TITRATION IN GLACIAL ACETIC ACID

The method described for determining amines on p. 488 can be used equally well for titration salts of carboxylic acids.

## CARBOXYLIC ACID ESTERS

### GENERAL METHOD USING SAPONIFICATION<sup>25</sup>

Esters may be very simply determined by saponification with standard alkali solutions. Any free acid or base in the sample should be determined beforehand.

*Procedure.*—A sample containing about 0.01 mole of ester is weighed into a 250-ml. glass-stoppered Erlenmeyer flask with a condenser to fit the ground joint for use with volatile or water-insoluble samples. To the sample is added 50 ml. of 0.5 *N* sodium hydroxide, aqueous if the sample is soluble in water or alcoholic if the sample is insoluble in water. The solution is heated for 2 hours on a steam bath (longer if the particular ester is difficultly saponifiable). The heating should be under reflux for volatile samples or if alcoholic sodium hydroxide is used. After the specified length of time, the excess alkali is titrated with standard 0.5 *N* acid, phenolphthalein indicator being used. Alkali resistant glassware should be used, especially in cases of low ester content. Lower concentrations of reagents can be used for low ester contents keeping in mind lower reactivity at the lower concentrations.

For esters that saponify with difficulty, amyl alcohol can be used as a solvent instead of methanol. Amyl alcohol has a higher boiling point, and this will accelerate the reaction. Potassium hydroxide should be used in amyl alcohol because it has a greater solubility than sodium hydroxide in this solvent. Also, concentra-

<sup>23</sup> Fritz, J. S., and Lisicki, N. M., *Anal. Chem.*, **23**, 589-591, 1951.

<sup>24</sup> Palit, S., *Ind. Eng. Chem., Anal. Ed.*, **18**, 246-251, 1946.

<sup>25</sup> Siggia, S., *Quantitative Organic Analysis Via Functional Groups*, 2nd Ed., John Wiley and Sons, Inc., New York, pp. 46-47, 1954. Reprinted with permission of the copyright owners.

tions of potassium hydroxide up to 5 *N* can be used for saponifying very stubborn esters. However, when this is done, the potassium hydroxide must be standardized each day and a blank should be heated for the same length of time as the sample, since some hydroxide is lost under these extreme conditions either by reaction with the glass or with some impurity in the amyl alcohol.

For samples insoluble in the alcoholic solvents alone, benzene can be included. It is a good idea to dissolve the sample in sufficient benzene that, when the alcoholic base is added, the sample will remain in solution. For titrating the excess base in this solvent system as well as in the amyl alcohol, a standard solution of hydrochloric acid in 1:1 ethylene glycol-isopropanol can be used. Phenolphthalein indicator can be used in most cases, but potentiometric titration with the glass and calomel electrodes can also be employed. These electrodes operate well in all these solvents except in the benzene-alcohol systems when the amount of benzene exceeds the amount of alcohol.

Calculations.—

Milliliters of acid to titrate 50 ml of the alkali  
— milliliters of acid for sample = *A*

$$\frac{A \times N \text{ acid} \times \text{mol. wt. ester} \times 100}{\text{Grams sample} \times 1000} = \% \text{ ester}$$

## CARBOXYLIC ACID AMIDES

### GENERAL METHOD BY TITRATION OF AMIDES AS BASES<sup>26</sup>

**Apparatus.**—A glass electrode (Beckman No. 4990-80) and a sleeve-type calomel electrode (Beckman No. 1170-71) were equilibrated by soaking in acetic anhydride for 12 hours prior to use. To minimize liquid junction potentials and to promote reproducibility, the aqueous bridge in the calomel cell was replaced with a 0.1 *M* solution of anhydrous lithium perchlorate in acetic anhydride. Lithium chloride proved to be too insoluble in acetic anhydride for use as a supporting electrolyte in the bridge solution.

**Reagents and Solutions.**—Lithium perchlorate, anhydrous salt, is available from the G. Frederick Smith Chemical Company, Columbus, Ohio.

**Acetic Anhydride.**—ACS reagent grade.

**Glacial Acetic Acid.**—ACS reagent grade.

**Dioxane.**—Purified by allowing to stand several days over NaOH, or by addition of LiAlH<sub>4</sub> and flask distilling (observe necessary cautions with LiAlH<sub>4</sub>).

**Perchloric Acid.**—70% vacuum distilled, available from the G. Frederick Smith Chemical Company, Columbus, Ohio.

**Perchloric Acid.**—A 0.1 *N* solution in acetic acid is prepared by dissolving approximately 9 ml. of 70% perchloric acid in acetic acid, adding 25 ml. of acetic anhydride, and diluting to 1 liter with acetic acid. The solution is allowed to stand 24 hours prior to use. The titrant is standardized either visually or potentiometrically against primary standard potassium acid phthalate dissolved in acetic acid.

**Perchloric Acid in Dioxane.**—This is prepared and standardized by the procedure of Fritz and may be used as an alternative titrant.

<sup>26</sup> Method of Wimer, D. C., *Anal. Chem.*, **30**, 77, 1958. Copyright 1958 by the American Chemical Society and reprinted with permission of the copyright owners.



**Procedure.**—A 0.006- to 0.009-mole sample is diluted to 100 ml. with acetic anhydride in a volumetric flask. A 10-ml. aliquot is transferred to a tall-form beaker, 100 ml. of acetic anhydride are added, and the titration is carried out with 0.1 *N* perchloric acid in acetic acid. The end point of the titration may be determined by inspection or by calculating maximum change in potential for small increments of perchloric acid added.

#### GENERAL METHOD BY SAPONIFICATION<sup>27</sup>

**Reagents.** Potassium Hydroxide.—1.0 *N* solution in ethylene glycol.

Hydrochloric Acid.—Standard 0.5 *N*.

Ethyl Ether, c.p.

Bromophenol Blue.—1.0% alcoholic solution.

**Procedure.**—Into each of two 250-ml. glass-stoppered Erlenmeyer flasks introduce exactly 50 ml. of the 1.0 *N* potassium hydroxide solution. Reserve one of the flasks as a blank. Into the other flask introduce an amount of sample, containing up to 6 milliequivalents of the amide. Fit each flask with a suitable reflux condenser and place the sample and blank on a hot plate. Bring the contents of the flasks to a boil and allow to reflux for 6 hours. Remove the flasks from the source of heat and rinse down the condenser with 25 ml. of distilled water, collecting the rinsings in the flask. Remove the condenser and add 30 ml. of ethyl ether to each flask. Add eight to ten drops of the bromophenol blue indicator and titrate with standard 0.5 *N* hydrochloric acid to a yellow-green end point. If acetanilide or acetotoluides are being analyzed, use thymol blue indicator and titrate from a yellow to a red end point.

**Calculation.**—

$$\frac{(A - B)N \times E.W.}{\text{Grams sample} \times 10} = \text{amide, \% by wt.}$$

where *A* = milliliters of *N* normal HCl required for the blank

*B* = milliliters of *N* normal HCl required for the sample

*E. W.* = equivalent weight of amide

**Discussion.**—Because of the excessive reaction time required and the possible loss of reagent by reaction with the glass container, determinations of amides using saponification reactions are seldom used. However, because of the limited number of procedures available for the determination, the method has value. In the case of primary amides where one of the hydrolysis products is ammonia, the saponification has been modified by evolving the ammonia formed into excess standard acid and the excess acid determined by titration.<sup>28</sup> Nitriles will interfere in this method.

#### GENERAL METHOD BY REDUCTION TO THE CORRESPONDING AMINE<sup>29</sup>

**Reagents.** Lithium Aluminum Hydride.—Ten grams of lithium aluminum hydride are refluxed with 500 ml. of anhydrous diethyl ether for several hours. If the

<sup>27</sup> Olsen, S., *Die Chemie*, 56, 202, 1943, as described by Hillenbrand and Pentz in *Organic Analysis*, Vol. III, Interscience Publishers, Inc., New York, p. 190, 1956.

<sup>28</sup> Siggia, S., *Quantitative Organic Analysis Via Functional Groups*, 2nd Ed., John Wiley and Sons, Inc., 1954, p. 47. Reprinted with permission of the copyright owner.

<sup>29</sup> Method of Siggia, S., and Stahl, C. R., *Anal. Chem.*, 27, 550-552, 1955. Copyright 1955 by the American Chemical Society and reprinted with permission of the copyright owners.

hydride is finely divided, it will dissolve in a relatively short time. Insoluble products, formed by the reaction of impurities in the ether with the lithium aluminum hydride, settle on cooling, and the clear solution can be pipetted off as needed. The solution should be protected from atmospheric moisture. The usable life of the solution is about one month.

**Sulfuric Acid.**—Standard 0.02 *N*.

**Sodium Hydroxide.**—Standard 0.02 *N*.

**Sodium Hydroxide.**—6 *N*.

**Methyl Purple Indicator.**—Fleisher methyl purple available from Burrell Corporation, Pittsburgh, Pa.

**Ethylene Glycol.**

**Isopropyl Alcohol.**

**Distillation Apparatus.**—The distilling apparatus used in Procedure A is the standard Kjeldahl steam distillation equipment.

The distilling apparatus in Procedure B consists of a 200-ml. round-bottomed

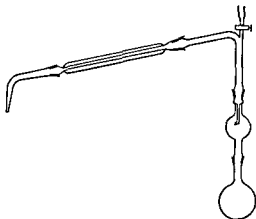


FIG. 19-1. Distillation Apparatus.

flask connected to a Kjeldahl bulb which is attached to a water condenser by a 75° connector. A stopcock and funnel are sealed on the connector at the bend so that ethylene glycol can be dropped into the flask (see Fig. 19-1).

**Procedure A.**—An exactly weighed sample containing approximately 0.0006 mole of amide is placed in a 100-ml. Kjeldahl flask, and 5 ml. of lithium aluminum hydride reagent are added. The solution is allowed to stand for 15 minutes at room temperature to ensure complete reduction of the amide, and the flask is then attached to the Kjeldahl distillation apparatus. A 200-ml. Erlenmeyer flask containing ex-

actly 50 ml. of 0.02 *N* sulfuric acid is placed on the apparatus, so that the end of the condenser is below the surface of the acid. Water is added dropwise to the reaction flask until the excess lithium aluminum hydride is decomposed. Ten milliliters of 6 *N* sodium hydroxide are added and steam distillation is carried out as in a Kjeldahl determination. About 50 ml. of distillate are collected in the 0.02 *N* sulfuric acid and the excess acid is titrated with standard 0.02 *N* sodium hydroxide to the green end point of methyl purple indicator. Per cent amide is calculated as follows:

$$\frac{\left\{ \begin{array}{l} \text{(Titration for 50 ml. of acid — titration for sample)} \\ \times N \text{ of NaOH} \times M.W. \text{ amide} \times 100 \end{array} \right\}}{\text{wt. of sample} \times 1000} = \% \text{ amide}$$

**Procedure B.**—A weighed sample containing approximately 0.0006 mole of amide is placed in a 200-ml. round-bottomed flask, and 10 ml. of lithium aluminum hydride reagent are added. The mixture is refluxed on a steam bath for 0.5 hour. The flask is cooled to room temperature and the excess reagent is decomposed by dropwise addition of water. After the reagent is completely decomposed the sides of the flask are washed with about 10 ml. of water, and 5 ml. of 6 *N* sodium hy-

droxide are added. A few boiling chips and 25 ml. of ethylene glycol are added before the flask is attached to the distilling apparatus. The solution is distilled at a rapid rate nearly to dryness and 25 ml. of ethylene glycol are added through the stopcock on the connector at such a rate that boiling does not stop. The addition and distillation of 25-ml. portions of ethylene glycol are continued until 100 ml. have been distilled. The condenser is washed with approximately 50 ml. of hot isopropyl alcohol, and the amine contained in the distillate and washings is titrated potentiometrically with 0.02 *N* sulfuric acid. Per cent amide is calculated in the following manner:

$$\% \text{ Amide} = \frac{\text{ml. of H}_2\text{SO}_4 \times N \text{ of H}_2\text{SO}_4 \times \text{mol. wt.} \times 100}{\text{Wt. of sample} \times 1000}$$

Nitriles constitute interferences in this method.

## CARBOXYLIC ACID CHLORIDES

### GENERAL METHOD INCLUDING DETERMINATION OF FREE HYDROCHLORIC ACID AND FREE CARBOXYLIC ACID ALONG WITH THE DETERMINATION OF ACID CHLORIDE<sup>30</sup>

**Reagents.** Acetone, c.p.

Anhydrous Diethyl Ether.

Chlorobenzene.

Sodium Hydroxide.—0.5 *N* and 0.1 *N*.

*N*-Tripropylamine in Chlorobenzene.—Standard 0.1 *N*.

*m*-Chloroaniline.—Freshly distilled.

The tripropylamine may be standardized against maleic acid dissolved in acetone or against a solution of dry hydrogen chloride in ether-chlorobenzene, which has been standardized by dissolving an aliquot in acetone-water and titrating with standard 0.1 *N* sodium hydroxide. If the maleic acid standardization is used, it should be remembered that only one carboxy group on the maleic acid can be titrated with tripropylamine.

**Procedures.** Method A.—An exactly weighed sample of acid chloride containing not more than 0.001 mole of hydrogen chloride is dissolved in a 1:1 mixture of ether-chlorobenzene and titrated potentiometrically (using glass or calomel electrodes) with standard 0.1 *N* tripropylamine in chlorobenzene, using a 10-ml. buret. Only the hydrogen chloride titrates and the break occurs between 350 and 150 mv. Per cent hydrogen chloride is calculated using the following equations:

$$\frac{\text{Ml.} \times N \text{ TPA}}{\text{Wt. of sample} \times 1000} = \text{mole of HCl per gram of sample}$$

$$\text{Mole of HCl per gram of sample} \times 100 \times 36.5 = \% \text{ HCl}$$

**Method B.**—A sample containing approximately 0.01 mole of acid chloride plus free carboxylic acid is weighed in a glass-stoppered weighing bottle or in a sealed ampoule. Sealed ampoules should be used for all volatile acid chlorides. The weighed sample is placed in a 250-ml. glass-stoppered flask containing 5 ml. of *m*-chloroaniline and 25 ml. of acetone. If the sample is weighed in a weighing bot-

<sup>30</sup> Stahl, C. R., and Siggia, S., *Anal. Chem.*, 28, 1971, 1956. Copyright 1956 by the American Chemical Society and reprinted with permission of the copyright owners.

tle, the stopper should be removed just before the sample is placed in the flask and the weighing bottle slid down the side of the flask, so that the sample and reagent do not mix. The flask is sealed with stopcock grease and is shaken to mix the sample and reagent. The contents of the flask are cooled slightly below room temperature in running tap water or in ice, and the flask is allowed to stand 5 minutes to ensure complete reaction.

After the reaction is complete, the stopper is removed and 5 ml. of distilled water are added. The stopper is replaced and the flask is shaken to dissolve the amine hydrochloride formed in the reaction. Then the contents of the flask are washed into a beaker with acetone. Using a pH meter equipped with a glass-calomel electrode system, standard 0.5 *N* sodium hydroxide is added from a buret until the pH of the solution is approximately 4. The volume of 0.5 *N* sodium hydroxide is read, then the solution is titrated potentiometrically with standard 0.1 *N* sodium hydroxide.

The first break, which occurs between pH 5 and 6, represents the neutralization of the amine hydrochloride formed by the reaction of the *m*-chloroaniline with the acid chloride and free hydrogen chloride. The equivalents of 0.1 *N* sodium hydroxide plus the equivalents of 0.5 *N* sodium hydroxide added, equal the equivalents of acid chloride plus hydrogen chloride in the sample. The second break occurs between pH 8 and 9.5 and represents the titration of the free carboxylic acid.

Two concentrations of standard sodium hydroxide are used. A rather large sample is required to obtain a sufficiently large titration for the free carboxylic acid, which is usually present in relatively small quantities. The total titration would be large if 0.1 *N* hydroxide were used, and the titration for free carboxylic acid would be small if 0.5 *N* hydroxide were used in the total titration. In this procedure, the bulk of the acidity is neutralized with 0.5 *N* reagent, and the 0.1 *N* hydroxide is used to carry the titration through the two neutral points. Per cent acid chloride is calculated as follows:

$$\frac{(\text{Ml. of } 0.5 \text{ } N \text{ NaOH} \times N) + (\text{ml. of } 0.1 \text{ } N \text{ NaOH} \times N)}{\text{Wt. of sample} \times 1000} = \text{moles of acid chloride} + \text{HCl per gram of sample}$$

$$\frac{(\text{Mole of acid chloride} + \text{HCl per gram}) - (\text{mole HCl per gram})}{= \text{mole acid chloride per gram}}$$

$$\text{Mole of acid chloride per gram} \times 100 \times \text{mol. wt. of acid chloride} = \% \text{ acid chloride}$$

Per cent free carboxylic acid is calculated using the following equation:

$$\frac{(\text{Ml. to second break} - \text{ml. to first break}) \times N \text{ of NaOH} \times \text{mol. wt. of acid} \times 100}{\text{Wt. of sample} \times 1000} = \% \text{ free carboxylic acid}$$

## CARBOXYLIC ANHYDRIDES

### GENERAL METHOD USING REACTION WITH ANILINE<sup>31</sup>

**Reagents.** Ethylene Glycol-isopropyl Alcohol Mixture.—1:1 by volume.

**Hydrochloric Acid.**—Standard 0.2 *N* in ethylene glycol-isopropyl alcohol mixture

<sup>31</sup> Siggia, S., and Hanna, J. G., *Anal. Chem.*, 23, 1717, 1951. Copyright 1951 by the American Chemical Society and reprinted with permission of the copyright owner.

(19 ml. of concentrated hydrochloric acid diluted to 1 liter with 1:1 ethylene glycol-isopropyl alcohol).

Aniline, c.p.

**Procedure.**—A sample containing approximately 0.004 mole of acid anhydride is accurately weighed in a 20 × 150 mm. test tube. If the sample contains an acid anhydride which requires heat for complete reaction, it is weighed in a 50-ml. condenser flask. Aniline is added to the sample drop by drop until 0.9 g. has been added. This is accurately weighed. The sample is allowed to stand in the test tube 5 minutes. The condenser flask is attached to a condenser in a reflux position and immersed in a beaker of boiling water for the required length of time. The reaction mixture is transferred quantitatively from the test tube or the condenser flask to a 150-ml. beaker with 1:1 ethylene glycol-isopropyl alcohol mixture. Ethylene glycol-isopropyl alcohol mix is added until the volume is approximately 50 ml. A pH meter is used to indicate the apparent pH after each addition of acid as the sample is titrated with 0.2 *M* hydrochloric acid prepared in the ethylene glycol-isopropyl alcohol mixture. The neutralization point is determined by plotting the apparent pH against milliliters of acid. A blank is run on the aniline by titrating an accurately weighed amount, approximately 0.4 g., potentiometrically with 0.2 *N* hydrochloric acid in the ethylene glycol-isopropyl alcohol mixture.

Calculations.—

$$\frac{(x - a) \times \text{normality of HCl} \times \text{mol. wt. of acid anhydride}}{1000 \times \text{wt. of sample}} \times 100 = \% \text{ acid anhydride}$$

when *a* equals milliliters of acid used to titrate excess aniline, and *x* equals milliliters of acid needed to titrate total amount of aniline used. The aniline used should not be assumed to be 100%, but should be assayed so that this value is a correct one. The aniline can be assayed by titration as described above.

Free carboxylic acids in the anhydrides do not interfere.

## UNSATURATED COMPOUNDS

### GENERAL METHOD BY BROMINATION<sup>32</sup>

**Reagents.**—

Bromate-Bromide Solution, 0.1 *N*.

Mercuric Sulfate, 0.2 *N*.—950 ml. water; 28 ml. conc. H<sub>2</sub>SO<sub>4</sub>; 30 g. HgSO<sub>4</sub>.

Carbon Tetrachloride, c.p.

Glacial Acetic Acid, c.p.

Potassium Iodide, 20%.

Sulfuric Acid, 6 *N*.

Sodium Thiosulfate, 0.05 *N*.

Starch Indicator Solution.

Sodium Chloride, 2 *N*.

**Procedure.**—Water-soluble samples are diluted to 0.08 *N* in unsaturation and a 25-ml. aliquot taken (0.002 equivalent in unsaturation).

Hydrocarbon-soluble samples are dissolved in carbon tetrachloride.

<sup>32</sup> Method of Lucas, H. H., and Pressman, D., *Ind. & Eng. Chem., Anal. Ed.*, **10**, 140-142, 1938, as described by Siggia, S., in *Quantitative Organic Analysis Via Functional Groups*, 2nd Ed., John Wiley and Sons, Inc., New York, pp. 69-71, 1954. Reprinted with permission of the copyright owner.

When volatile, the sample is weighed in a sealed glass ampoule and placed in a volumetric flask of convenient volume to give a 0.08 *N* solution in terms of unsaturation, along with enough carbon tetrachloride or water to cover the ampoule. The volumetric flask is chilled in ice water, and the ampoule is then broken with a glass rod. The rod is rinsed with chilled carbon tetrachloride or water, and the solution is made up to the mark with the same chilled solvent. To pipet a sample of this solution, vacuum should not be applied. Instead, the pipet is equipped with a 2-hole rubber stopper to fit the volumetric flask, and a piece of glass tubing is inserted in the other hole. The solution is then blown into the pipet by compressed air or by mouth.

A calculated excess (10 to 15%) of 0.1 *N* bromate-bromide solution (about 25 ml.) is introduced into a 250- to 300-ml. Erlenmeyer flask having a glass stopper equipped with a sealed-in three-way stopcock (see Fig. 19-2). If the amount of unsaturation in the sample is unknown, a preliminary analysis is made with a large excess of bromate-bromide solution. From this result the desired excess can be calculated. The reason for avoiding the large excess is to minimize substitution, which leads to high results. If the excess is less than 10 to 15%, the addition proceeds so slowly toward the end of the bromination that the bromination may not be complete in the specified time.



Fig. 19-2. Bromination Apparatus.

After the addition of the bromate-bromide solution the flask is evacuated through tube *A* with a water aspirator, and 5 ml. of 6 *N* sulfuric acid is added by means of the funnel attachment *B* on the stopper, 2 or 3 minutes being allowed to elapse for the bromine to be liberated. Next, 10 to 20 ml. of 0.2 *N* mercuric sulfate is added, followed by the sample containing solution (25 ml. of the sample solution should be used if the concentration is 0.08 *N* with respect to unsaturation). Water or carbon tetrachloride, depending on which was used to dissolve the sample, should be used to rinse the sample into the flask. A total of 15 ml. of wash liquid in three portions should be employed. In the case of samples dissolved in carbon tetrachloride, 20 ml. of glacial acetic acid is added. When the samples are dissolved in water the acetic acid is omitted. The flask is then wrapped in black cloth and is shaken for 7 minutes (time may vary with some samples). Then 15 ml. of 2 *N* sodium chloride and 15 ml. of 20% potassium iodide are added and the flask shaken for about one-half minute. The vacuum is broken, and the free iodine is titrated with 0.05 *N* sodium thiosulfate, starch indicator being used. A blank, with about one-third the amount of bromate-bromide solution used in the analysis, is run under the same conditions as the samples.

#### Calculations.—

$$\frac{(\text{Ml. for blank} - \text{ml. for sample}) \times N \text{ thiosulfate} \times \text{mol. wt. compound} \times 100}{\text{Grams sample} \times 2000 \times B} = \% \text{ compound}$$

*B* = number of moles bromine absorbed by compound being determined

**Discussion.**—The molar ratio of mercuric ion to bromide ion should be greater than one if the mercuric salt is to have sufficient catalytic effect. Sodium chloride

is necessary to liberate free bromine from its complex with mercuric sulfate. Acetic acid is necessary to solubilize the unsaturated compound in the water layer.

The 7-minute shaking is enough for most samples, but some samples require a longer time. Maleic and fumaric acids in water require one-half hour in the presence of mercuric sulfate for complete reaction.

Cinnamic acid requires no mercuric sulfate for quantitative results; in fact, mercuric sulfate is detrimental since it causes substitution. Propiolic acid, dimethylbutadiene, and propargyl alcohol substitute bromine and yield high results when determined by this method. Because of varying amounts of substitution for different compounds, it is difficult to ascribe a general accuracy and precision value to this procedure.

Absorbed oxygen in solutions of alkynes and exposure to sunlight generally affect results significantly.

Interfering substances consist of phenols and amines, which substitute bromine and also hydrazines, some aldehydes, and other materials which are oxidized by bromine. The analyst must be alert for substitution reactions which will yield high values for unsaturation.

### GENERAL METHOD BY IODINE NUMBER <sup>33</sup>

There are instances when the preceding bromination procedure for determining unsaturated compounds cannot be used because the bromine not only adds on the unsaturated linkage but also substitutes some of the hydrogen atoms on the components in the sample.

**Reagents.** **Hanus Iodine Monobromide Solution.**—13.6 g. of c.p. iodine are dissolved in 825 ml. of glacial acetic acid by warming and stirring. The solution is cooled, and 25 ml. are pipetted out, diluted to about 200 ml., and titrated with 0.1 *N* thiosulfate.

Three milliliters of c.p. bromine are added from a buret to 200 ml. of glacial acetic acid, mixed well, and 5 ml. are pipetted out. This is diluted to about 150 ml. with water, and 10 ml. of 15% potassium iodide solution is added. The liberated iodine is titrated with 0.1 *N* sodium thiosulfate. The titration for the 5 ml. of bromine solution should be approximately 80% of the titration of the 25 ml. of the iodine solution.

The amount of bromine solution to be added to the remaining 800 ml. of iodine solution is calculated as follows:

$$800 \times \frac{\text{Titration of iodine solution}/25}{\text{Titration of bromine solution}/5}$$

After mixing, the solution is diluted to 1 liter with acetic acid and stored in a glass-stoppered amber bottle. A blank should be run with each determination or with each set of determinations, if more than one sample is run at one time.

**Sodium Thiosulfate.**—Standard 0.1 *N*.

**Potassium Iodide Solution,** 15%

**Starch Indicator Solution.**

**Procedure.**—A sample is taken of such a size that titration of the sample solution will be at least 60% that of the blank. If the sample titration comes to less than

<sup>33</sup> Hanus method is described in Snell, F. D., and Biffen, F. M., *Commercial Methods of Analysis*, McGraw-Hill Book Co., Inc., New York, pp. 345–346, 719, 1944. Reprinted with permission of the copyright owner.

60% of that of the blank, not enough reagent is present for complete reaction, and the analysis should be repeated with a smaller sample.

The sample is dissolved in chloroform or carbon tetrachloride using a 250-ml. iodine flask. If warming is necessary to dissolve the sample, the solution should be cooled to room temperature before the Hanus solution is added. The same volume of solvent is put in a separate flask. Into each of these flasks is pipetted 25 ml. of Hanus solution, and the flasks are shaken to ensure homogeneity. The samples are allowed to stand for exactly 30 minutes with occasional shaking. After that time, 50 to 100 ml. of water are added, and also 10 ml. of 15% potassium iodide solution. The liberated iodine is titrated with 0.1 *N* thiosulfate until the iodine color has almost disappeared. One milliliter of starch indicator is added, and the titration is continued until the blue color is discharged. The flask should be agitated quite vigorously when the reaction is near the end point to ensure extraction of all the iodine from the organic layer.

**Calculations.**— $\text{Ml. of thiosulfate for blank} - \text{ml. of thiosulfate for sample} = A$

$$\frac{A \times N \text{ thiosulfate} \times 126.9 \times 100}{\text{Grams sample} \times 1000} = \% \text{ iodine} = \frac{\text{centigrams iodine}}{\text{gram sample}}$$

(The calculation is given in these arbitrary units because this procedure is used mostly on hydrocarbons, fatty acids, and esters where no clean-cut compound exists but a mixture of unsaturated compounds is present. There is no conclusive molecular weight which can be used in these cases. When definite compounds are being determined, substitute the molecular weight of the compound for the 126.9, and divide by 2 for each double bond present since 2 equivalents of iodine are involved per double bond. The equation will then yield the per cent compound.) Any compound which is readily oxidized will also give erroneous results.

It was found advisable to check each new batch of Hanus solution against a standard to ensure proper preparation. Corn oil was used because of its stability and because it is so readily adapted to this procedure.

### GENERAL METHOD BY HYDROGENATION<sup>34</sup>

**Procedure.**—About 3 ml. of solvent and about 0.5 g. of catalyst are added to the hydrogenation vessel. The amount of catalyst is not critical. If a larger amount of catalyst is used, the hydrogenation of the compound proceeds more rapidly. The time required to saturate the catalyst, however, is much longer, so that no time is saved. When a small amount of catalyst is used, the sample hydrogenates more slowly, but the time is saved in saturating the catalyst.

A weighed sample which will consume about 0.0002 mole of hydrogen is put in the cup indicated by *A* in Fig. 19-3. If the sample is a solid it is weighed in a small aluminum boat or envelope. The boat is placed in the cup. Liquid samples are weighed in small glass receptacles or in gelatin capsules. (When using capsules, water must be used as the solvent.) All joints and stopcocks should be well greased to prevent hydrogen leakage.

The system is flushed with a slow stream of hydrogen for 3 to 5 minutes, introducing the hydrogen through stopcock at *B*, which is in position as indicated; the mercury level is as near the stopcock as possible. The hydrogen is allowed to

<sup>34</sup> Siggia, S., *Quantitative Organic Analysis Via Functional Groups*, 2nd Ed., John Wiley and Sons, Inc., New York, pp. 74-77, 1954. Reprinted with permission of the copyright owner.



escape through stopcock *C*. After 3 to 5 minutes stopcock *C* is closed and the mercury is lowered to a position well below the calibrations on the buret. Then stopcock *B* is turned to position *D* and the hydrogen is disconnected.

A pressure of about 3 cm. of mercury is applied and the stirrer started. Stirring is brought about by a rotating magnet under the reaction flask with a small glass-covered iron paddle inside the flask. These magnetic stirrers can be purchased or they can be improvised by attaching a magnet to the shaft of a stirring motor. The more vigorous the agitation, the more rapidly will the catalyst be saturated and the sample hydrogenated. When the mercury level ceases to rise, it signifies that the catalyst is saturated. The leveling bulb is then raised and stopcock *C* is opened slowly, allowing hydrogen to escape until the mercury level is within the calibrations on the gas buret. The stopcock is again closed, and about 5 to 10 minutes are allowed for the apparatus to come to equilibrium. The buret reading and the temperature are noted. The sample is then allowed to fall into the solvent by turning *A*. About 3 cm. of pressure is applied as agitation is continued, until the level of the mercury ceases to rise. The buret reading is taken and 3 cm. of pressure again applied for 10 minutes to ensure complete reaction. The temperature is again noted.

For accurate results, the volume of the apparatus is needed to correct hydrogen-volume readings when the temperature at the end of an analysis is different from the temperature at the beginning. If this is not done the volume readings will be in error because of expansion or contraction of the hydrogen in the free space of the apparatus.

The volume of the apparatus is measured by completely filling it (up to the top mark on the buret) with water and then weighing the water. The correction is made by adding the volume of the apparatus to the volume between the top mark and the level of the mercury at the end of the hydrogenation minus the volume of solvent used. This equals the volume of free space at the end of the hydrogenation. This volume is corrected for temperature changes which may have occurred during the determination by the following equation:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (T = \text{absolute temperature})$$

The difference between the volume before the temperature correction and the volume after the correction is the volume change due to expansion or contraction of the gas in the apparatus. This volume change is either added to, or subtracted from, the volume of hydrogen consumed as read on the burets, depending on

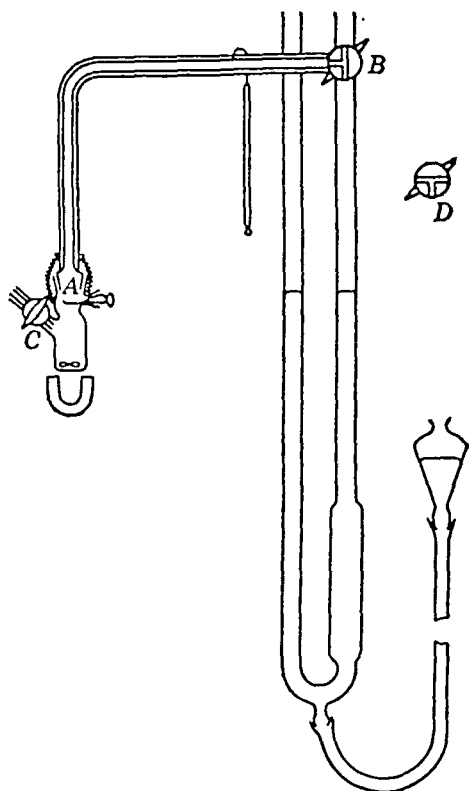


FIG. 19-3. Quantitative Hydrogenation Apparatus.

whether the final temperature was lower or higher than the initial gas temperature.

Low-boiling solvents are to be avoided because temperature changes affect the vapor pressure of the solvent. Since the low-boiling solvents exhibit significant variations in vapor pressure over the range of temperatures encountered in the room, significant errors can result in the volume measurements.

In this procedure a 7-ml. buret is used. Results have an accuracy and precision of  $\pm 5\%$ . If a 50-ml. gas buret is used and the sample is five to eight times larger (the remainder of the apparatus remaining exactly the same), the results will be accurate and precise to  $\pm 1$  to  $2\%$ .

Oxygen should be completely eliminated from the apparatus since it will consume hydrogen. Any other materials which can be reduced with hydrogen will, of course, interfere.

Calculations.—

Volume of hydrogen consumed (corrected for any temperature fluctuations) =  $V_t$

Volume of hydrogen converted to  $0^\circ\text{C.} = V_0$

The temperature of the experiment =  $T^\circ\text{C.} + 273$

The temperature at  $0^\circ\text{C.} = 273$

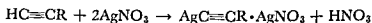
$$\frac{V_t}{T^\circ\text{C.} + 273} = \frac{V_0}{273}$$

$$\frac{V_0/22,400}{\text{Grams sample/mol. wt. sample}} = \frac{\text{moles hydrogen consumed}}{\text{mole sample}}$$

**Caution.**—All Raney nickel should be stored under alcohol (preferably a high-boiling alcohol). Dry Raney nickel will react with atmospheric oxygen, emitting sparks which can ignite any surrounding combustible material. The presence of hydrogen increases the hazards. None of the catalyst should be allowed to dry in the apparatus, on the desk top, or on the implements used to introduce the catalyst into the apparatus.

Adam's catalyst when dry will glow in the presence of hydrogen and oxygen. Hydrogen is adsorbed on the catalyst and reacts with oxygen, emitting much heat. When the catalyst is put in the apparatus, it should be completely wet with solvent. Any dry particles of catalyst will glow as soon as the hydrogen is introduced, causing either the solvent vapors to flash or the hydrogen-air mixture to explode.

### GENERAL METHOD FOR DETERMINING ACETYLENIC HYDROGEN COMPOUNDS ( $\text{HC}\equiv\text{C}-$ )<sup>35</sup>



**Reagents.** Sodium Hydroxide, 0.02 *N.*—For samples containing less than 1% acetylenic compound.

Sodium Hydroxide, 0.1 *N.*—For samples containing more than 1% acetylenic compound.

**Silver Nitrate Solution.**—100 g. of silver nitrate dissolved in water and diluted to 1 liter (store in dark bottle). For the working solution, 35 ml. of the aqueous silver nitrate solution is diluted to 140 ml. with 95% ethanol.

<sup>35</sup> Method described by Altieri, V. J., *Gas Analysis and Testing of Gaseous Materials*, American Gas Assoc., Inc., pp. 330–332, 1945. Reprinted with permission of the copyright owners.

**Indicator.**—Alcoholic solution composed of a mixture of 0.1% methyl red and 0.05% methylene blue. Store in a dark dropping bottle.

**Procedure.**—In a 250-ml. Erlenmeyer flask 50 ml. of silver nitrate solution is placed together with the sample, which should contain 0.002 equivalent of acetylenic hydrogen if the 0.1 *N* sodium hydroxide is to be used in the final titration; or 0.0004 equivalent of acetylenic compound if the 0.02 *N* sodium hydroxide is to be used.

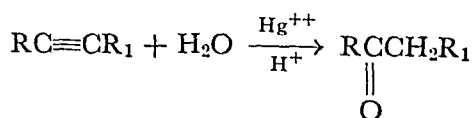
About six drops of indicator are added, and the contents of the flask are titrated with the sodium hydroxide solution of appropriate strength. The end point is the change of the red color of the indicator to a dull yellow.

The above procedure is accurate and precise to  $\pm 0.5$  to 1.0%. It was tested with 3-butyne-1-ol; ethynylcyclohexanol, 1-hexyne and 3-butyne-2-ol. Any acidic or basic materials in the sample will interfere; they should be determined on a separate sample, and the proper correction applied to the acetylenic hydrogen result. Aldehydes or other reducing substances interfere by reducing the silver ions to metallic silver, which darkens the solution to such a degree as to completely obscure the end point. Also, the acids formed on the oxidation of the aldehyde would interfere even if the metallic silver formed did not obscure the end point.

**Caution.**—Silver salts of acetylenic compounds are explosive when dry. Destroy these salts by dissolving in dilute nitric acid; or by making the solution ammoniacal and dissolving the silver acetylide with 5% potassium cyanide (Hood). The resulting solution is poured into 5% ferrous sulfate to destroy the excess cyanide.

## GENERAL METHOD FOR DISUBSTITUTED ACETYLENIC COMPOUNDS $RC\equiv CR_1$ BY HYDRATION <sup>36</sup>

This method is based on the reaction



and determination of the ketone formed.

**Reagents.** Hydroxylamine Hydrochloride, 0.5 *N*.—In 1 to 1 methanol-water.

The catalyst is made from 0.5 g. of mercuric sulfate, 2 ml. of sulfuric acid, and 63.4 ml. of water.

**Alcoholic Sodium Hydroxide, 1.0 *N*.**—Sodium hydroxide is dissolved in as little water as possible. The sodium carbonate is filtered off, and the solution is diluted with methanol to the desired volume. This solution need not be standardized.

**Aqueous Sodium Hydroxide.**—Standard 0.5 *N*.

**Apparatus.**—Glass and calomel electrodes, with a Model H-2 Beckman pH meter.

**Procedure.**—A sample containing 0.05 to 0.20 mole of acetylenic compound is dissolved in methanol and diluted to 100 ml. in a volumetric flask; 10-ml. aliquots are used for the determinations.

Ten milliliters of sample solution are added to 20 ml. of catalyst in a 200-ml.

<sup>36</sup> Method of Siggia, S., *Anal. Chem.*, 28, 1483, 1956. Copyright 1956 by the American Chemical Society and reprinted with permission of the copyright owner.

three-necked flask connected to a reflux condenser. Glass stoppers are inserted in the two unused necks of the flask. The mixture is refluxed for 1 hour and then cooled in ice with the condenser still attached. After cooling, the condenser is washed with 10 ml. of 1 to 1 methanol-water and allowed to drain. The flask is disconnected from the condenser and glass-calomel electrodes are inserted into the flask through the two side necks. The acid is just neutralized (pH 7) with 1.0 *N* alcoholic sodium hydroxide.

Fifty milliliters of hydroxylamine hydrochloride are added, the mixture is again refluxed for 1 hour and cooled in ice, and the condenser is washed with 1 to 1 methanol-water. The mixture is transferred to a 400-ml. beaker, using 50 ml. of 1 to 1 methanol-water to wash the flask. As much of the solid residue as possible is left in the flask during transfer.

The liberated hydrochloric acid is titrated potentiometrically with standard 0.5 *N* sodium hydroxide, using the glass and calomel electrodes. The end point is determined from a plot of milliliters of reagent vs. pH.

If carbonyl compounds are present in the sample, they should be determined using the hydroxylamine hydrochloride analysis on an unhydrated sample.

Calculation.—

$$\frac{\text{Ml. NaOH} \times N_{\text{NaOH}} \times \text{mol. wt. compound} \times 100}{\text{Wt. sample} \times 1000} = \% \text{ acetylenic compound}$$

## 2,4-DINITROPHENYLHYDRAZONE METHOD

*Reagents.*—Catalyst as described above.

A saturated solution of 2,4-dinitrophenylhydrazine at 0°C. in 2 *N* hydrochloric acid.

*Procedure.*—A sample is dissolved in methanol and diluted to 100 ml., so that a 10-ml. aliquot contains approximately  $4 \times 10^{-4}$  mole. Ten milliliters of sample are added to 20 ml. of mercuric sulfate-sulfuric acid catalyst and refluxed for 1 hour in a three-necked flask with glass stoppers in the two unused necks. After the hydration reaction period, the flask is cooled in ice with the condenser attached, and the condenser is washed with 10 ml. of 1 to 1 methanol-water. At this point there is a white precipitate in the flask, which does not appear to affect the results.

With the condenser still in position, hydrogen sulfide is passed into the solution to precipitate mercury as the sulfide. When this reaction is complete (5 to 10 minutes), the sulfide is filtered off through a No. 30 Whatman filter paper and the flask and paper are washed with a 1 to 1 solution of methanol-water.

To the filtrate are added 50 ml. of 2,4-dinitrophenylhydrazine solution, and the mixture is allowed to stand one-half to 1 hour. The resulting solution is warmed on a hot plate with constant stirring to coagulate the precipitate. When the supernatant liquid is clear, the precipitate is filtered off through a Gooch crucible with an asbestos mat, washed with water, dried at 100°C., and weighed. If the resultant hydrazone exhibits a significant solubility with the alcohol present (this must be predetermined), the solution is boiled for a few minutes to remove as much alcohol as possible before filtration. Acetylenic compounds containing hydroxyl groups cannot usually be determined by this method, because of the solubilizing effects of these groups.

Free carbonyl compounds in the sample will interfere unless a correction is applied.

## Calculations.—

$$\frac{\text{Wt. hydrazone}}{\text{Wt. sample}} \times \text{gravimetric factor} \times 100 = \% \text{ acetylenic compound}$$

## ETHERS

ALKOXYL—ACIDIMETRIC DETERMINATION<sup>37</sup>

This method applied for methoxyl through butoxyl determinations.

**Apparatus and Reagents.** Alkoxy Apparatus.—A diagram of this apparatus is shown in Fig. 19-4. Any conventional alkoxy apparatus may also be used, although the scrubber is superfluous.

**Tetrabutylammonium Hydroxide, 0.02 N.**—Tetrabutylammonium hydroxide, 0.1 N, in 10 to 1 benzene-methanol. Dissolve 80 grams of tetrabutylammonium iodide (obtained from Rymark Laboratories, Terre Haute, Ind.) in 180 ml. of reagent grade absolute methanol. Place in an ice bath, add 40 grams of finely ground silver oxide, stopper the flask, and agitate intermittently for 1 hour. Filter through a sintered-glass funnel of fine porosity, rinse the flask, and precipitate with three 50-ml. portions of cold benzene and add to the filtrate. Dilute the filtrate to 2 liters with dry benzene. Add 20 ml. of methanol to 200 ml. of this solution and dilute to 1 liter with benzene.

**Pyridine.**—Flash-distill technical grade pyridine from barium oxide using an upright condenser, discarding the first and last 10% of the distillate.

**Hydriodic Acid.**—Merck & Company, Inc., reagent grade, 55 to 58% HI, specific gravity 1.7. No additional purification is necessary.

**Azo Violet Indicator Solution.**—Dissolve 0.5 g. of *p*-nitrobenzeneazoresorcinol in 100 ml. of pyridine.

**Xylene.**—Analytical reagent grade.

**Procedure.**—Accurately weigh 10 to 15 mg. of the solid alkoxy compound and transfer to the reaction flask. Weigh volatile samples in gelatin capsules. Add 0.5 ml. of xylene to the flask and dissolve the solid samples, heating if necessary. Add 5.0 ml. of hydriodic acid and a few boiling stones. Lightly grease the standard-

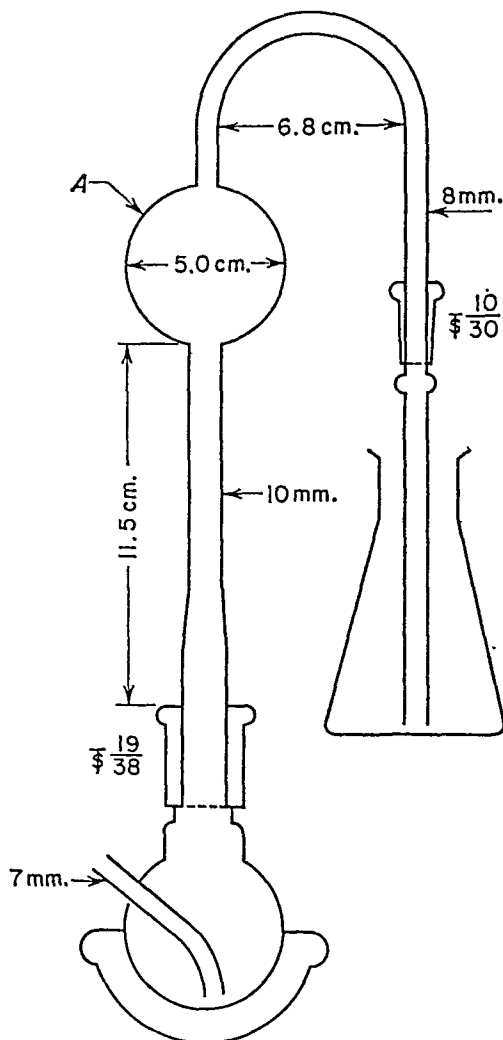


FIG. 19-4. Alkoxy Apparatus.

<sup>37</sup> Cundiff, R. H., and Markunas, P. C., *Anal. Chem.*, **33**, 1028, 1961. Copyright 1961 by the American Chemical Society and reprinted with permission of the copyright owner.

taper joints and connect the flask to the apparatus. Place 50 ml. of pyridine in an Erlenmeyer flask and allow the delivery tip to extend below the surface of the solvent. Pass nitrogen through the system, adjusting the initial rate to one bubble per second. Apply heat with a heating mantle, and adjust the heat so that the top of the condensate is just above bulb *A*. Continue this nitrogen rate for 20 minutes, then increase the rate to 2 to 3 bubbles per second for the remainder of the reaction period. Allow a minimum amount of condensate to pass into the receiver and, if fuming is observed in the receiver, lower the nitrogen rate and adjust the heat so that fuming is minimized. Continue the reaction an additional 25 minutes for methoxyl determination, an additional 40 minutes for ethoxyl determination, an additional 100 minutes for propoxyl and butoxyl determination, and an additional 160 minutes for *S*-methyl determination. Disconnect the Erlenmeyer flask and rinse the exit tube with pyridine, adding the washings to the receiving flask.

Gently boil the pyridine solution 2 minutes, cool, then titrate. The titration may be performed potentiometrically or as follows: Add two drops of azo violet indicator solution to the pyridine solution and titrate under nitrogen to a red end point, record the volume, then titrate to a violet end point. The volume difference between the red and violet end points is a measure of the alkoxy content.

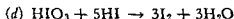
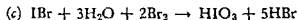
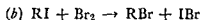
Perform blank analyses with each change of reagents, and subtract the volume difference between the red and violet end points from that obtained in the sample analysis.

Calculations.—

$$\frac{\text{Ml. TBAH} \times N_{\text{TBAH}} \times -\text{OR} \times 100}{\text{Wt. sample} \times 1000} = \% -\text{OR}$$

### ALKOXYL—IODIMETRIC <sup>38</sup>

This method applies only for methoxyl and ethoxyl determinations.



**Reagents.** Potassium Acetate in Acetic Acid.—Dissolve 100 g. of c.p. anhydrous potassium acetate in 1 liter of solution containing 900 ml. of glacial acetic acid and 100 ml. of acetic anhydride.

**Bromine Solution.**—Dissolve 1 ml. of bromine in 29 ml. of the above potassium acetate reagent. This solution should be prepared fresh daily.

**Sodium Acetate.**—Dissolve 250 g. of c.p. anhydrous sodium acetate in 1 liter of distilled water.

<sup>38</sup> Method as described by Niederl and Niederl, *Micromethods of Quantitative Organic Analysis*, 2nd Ed., John Wiley and Sons, Inc., New York, pp. 239-244, 1942. Reprinted with permission of the copyright owner.

**Aqueous Red Phosphorus Suspension.**—Suspend 30 g. of c.p. red phosphorus in 50 ml. of 5%  $\text{CdSO}_4$ .

**Potassium Iodide**, c.p.

**Formic Acid.**—Reagent grade, 90% sp. gr. 1.20.

**Hydriodic Acid.**—C.p. constant boiling mixture, b.p.  $126^\circ$  to  $127^\circ\text{C}$ . (57% hydriodic acid).

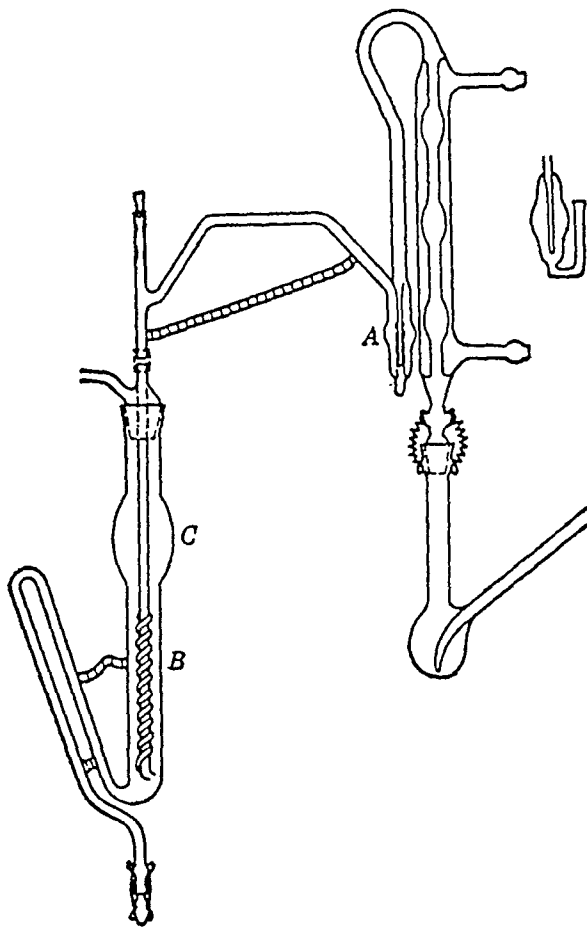


FIG. 19-5. Methoxyl-Ethoxyl Apparatus.

**Sulfuric Acid, 10%.**—Add 60 ml. of concentrated sulfuric acid to 940 ml. of distilled water.

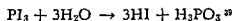
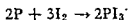
**Sodium Thiosulfate.**—Standard 0.1 *N*.

**Starch Indicator.**

**Carbon Dioxide.**—A commercial cylinder with a reducing valve is a good source.

**Apparatus (Fig. 19-5).**—Complete apparatus can be purchased from Scientific Glass Apparatus Company, Bloomfield, New Jersey, Catalog M-1745.

**Procedure.**—The trap (*A*) is two-thirds filled with the red phosphorus suspension. The phosphorus trap is to keep any free iodine from getting into the receiver. The  $\text{CdSO}_4$  is to remove any hydrogen sulfide formed.



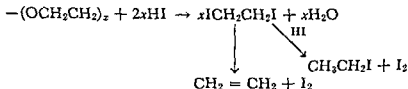
The receiver (B) is filled to a level representing one-third of the bulb portion (C) with bromine solution. The sample is placed in the reaction vessel together with a boiling chip and a crystal of phenol. Liquid samples should be weighed in gelatin capsules. To the sample is added 6 ml. of constant boiling hydriodic acid, the reaction flask is immediately attached to the condenser, and the joint is moistened with hydriodic acid. Water is circulated through the condenser, and the reaction flask is heated. A slow stream of carbon dioxide is bubbled through the solution at a rate of about 2 bubbles per second. An oil bath at 130° to 150°C. or a hot-spotter can be used as the heating element. After 45 minutes (1 hour for ethoxyl determination) the contents of the receiver are quantitatively transferred to a 500-ml. flask containing 10 ml. of sodium acetate solution. The solution is diluted to about 125 ml. with water, and formic acid is added dropwise until the bromine color is discharged; then three additional drops are added. After the solution stands 3 minutes, 3 g. of potassium iodide and 15 ml. of 10% sulfuric acid are added. The liberated iodine is titrated with 0.1 *N* sodium thiosulfate, starch indicator being used. A blank should be run on the phenol alone. In most cases, however, the blank is so small as to be unnecessary.

In a few cases the sample is not attacked completely by the hydriodic acid. This is probably due to insolubility in the acid. In these cases, a 1:1 phenol-hydriodic acid mixture should be tried.

**Calculations.**—

$$\frac{\text{Ml. thiosulfate} \times N \text{ thiosulfate} \times \text{mol. wt. alkoxyl group} \times 100}{\text{Grams sample} \times 6000} = \% \text{ alkoxyl}$$

**METHOD FOR OXYALKYLENE GROUPS  $\text{R}(\text{OCH}_2\text{CH}_2)_x\text{OR}_1$**   
 WHERE  $x$  CAN BE 1 OR GREATER AND  $\text{R}$  AND  $\text{R}_1$   
 CAN BE HYDROGEN ATOMS OR ALKYL, ARYL,  
 OR ACYL GROUPS<sup>40</sup>



**Reagents.** Hydriodic Acid.—55 to 58%, specific gravity 1.7 as used for methoxyl determinations is required. It is preferable to use hydriodic acid with as little free iodine as possible, in order to obtain low blanks and results with optimum precision and accuracy. Freshly opened bottles of hydriodic acid have a free iodine content equivalent to 2 to 4 ml. of 0.1 *N* thiosulfate per 5 ml. of hydriodic acid. The free iodine increases rapidly once the bottle is opened and it is not advisable to use acid with a free iodine content equivalent to over 10 ml. of 0.1 *N* thiosulfate per 5 ml. of acid. This impure acid will cleave the ether and ester link-

<sup>39</sup> Samuel and McHard, *Ind. Eng. Chem., Anal. Ed.*, 14, 754, 1942.

<sup>40</sup> Siggia, S., Starke, A. C., Garis, J. J., and Stahl, C. R., *Anal. Chem.*, 30, 115, 1958. Copyright 1958 by the American Chemical Society and reprinted with permission of the copyright owners.



ages and can be used, but the high blanks prevent optimum results. Hydriodic acid can be distilled to lower its free iodine content; however, it was found more expedient to purchase the acid in 0.25-pound bottles. Each bottle lasts for a few determinations and not enough time elapses for the blank to become excessive. Hydriodic acid containing hypophosphorus acid as a stabilizer must not be used.

**Aqueous Potassium Iodide Solution, 20%.**

**Standard Sodium Thiosulfate, 0.1 N.**

**Carbon Dioxide.**—Cylinder gas or dry ice in a Dewar flask can be used. Unopened cylinders should be rapidly vented to the atmosphere until frost forms on the nozzle of the valve. This reduces the oxygen content of the remaining gas and results in lower blanks.

**Procedure.**—Into a 50-ml. round-bottomed flask is pipetted 5 ml. of hydriodic acid. The flask contains a ground-glass joint to accommodate a vertical condenser, and is equipped with a side arm through which carbon dioxide can be passed to blanket the solution. A weighed sample containing 0.001 to 0.002 mole of oxyalkylene group is added to the hydriodic acid. The sample is best weighed in a tared glass thimble (1-ml. beaker works well) and then is dropped into the acid, thimble and all. The vertical condenser is connected with a thin grease seal at the outermost edge to cause a good seal. Too much grease should be avoided, as iodine tends to dissolve in the excess grease.

The flow of carbon dioxide is commenced and kept at a rate of a few (1 to 5) bubbles per second. A bubbler must be used in the carbon dioxide line, in order to avoid excessive amounts of gas, and to prevent iodine from being swept out of the system, causing low results. The system has to be kept under an atmosphere of carbon dioxide to avoid air oxidation of the iodide ion to free iodine, which would yield high, irreproducible blanks. After allowing a few minutes for the system to be covered with a blanket of carbon dioxide, heating is commenced. The sample solution is boiled gently for 90 minutes; vigorous boiling causes loss of iodine through the condenser. Ninety-minute boiling was sufficient for the most stubborn compounds encountered in this study; 45 minutes was satisfactory for ethylene glycol.

Concurrent with the sample is run a blank in the same manner and in duplicate equipment. A glass bead is included in the blank to avoid bumping. Carbon dioxide from the same source is fed into the system containing the blank. The blank is heated for the same length of time, because the blank is sizable and variation must be kept at a minimum for optimum results. It was found advantageous from a time standpoint to run several samples at one time, along with one blank. These are all heated at one time, by using a manifold of glass tubing to deliver the carbon dioxide from one cylinder. The use of one cylinder is emphasized, as carbon dioxide from cylinders contains oxygen which affects the blank. Different cylinders would contain different amounts of oxygen.

After the 90-minute boiling period, the walls of the condenser are washed down with 15 ml. of 20% potassium iodide solution. All crystals of iodine which may have formed in the condenser must be dissolved by the potassium iodide. The condenser is then washed with two 10-ml. portions of water and is disconnected from the flask. The tip is rinsed, and this washing is added to the flask. The contents of the flask are washed into an Erlenmeyer flask and titrated with 0.1 N thiosulfate to the disappearance of the iodine color. Some samples which contain large organic nuclei leave a tarry residue as a button. This is visible either in the titration flask or in the reaction flask. This residue usually contains a meas-

urable amount of iodine dissolved in it. This button should be dissolved in methanol and any iodine present should be titrated with thiosulfate. This increment is added to the original titration.

**Calculation.**—

$$\frac{(\text{Ml. sample} - \text{ml. blank}) \times N \text{ thiosulfate} \times (\text{OCH}_2\text{CH}_2)}{\text{Wt. sample} \times 20} = \% (\text{OCH}_2\text{CH}_2)$$

## AMINES: GENERAL METHOD BY TITRATION

### TITRATION IN GLYCOL-ISOPROPANOL <sup>41</sup>

Aliphatic amines can generally be titrated directly in aqueous solution with standard acid. If the amine is water insoluble, an excess of standard acid can be added and the excess acid back-titrated. Aromatic amines cannot be handled conveniently in this manner since they are very weak bases and yield very poor titration curves and, of course, no distinct indicator changes.

However, aromatic amines (including naphthylamines) and other weak organic bases such as pyridine and quinoline can be titrated nicely when dissolved in 1:1 ethylene glycol-isopropanol and titrated with 0.5 or 1.0 *N* hydrochloric acid made up with the glycol-isopropanol solvent (the regular concentrated hydrochloric acid is used to make up the solution; anhydrous acid is not needed). The titration curves obtained in this solvent <sup>41</sup> yield much sharper breaks than those for the same amine in an aqueous system. For some amines, even indicators can be used. High degrees of accuracy and precision ( $\pm 0.05$  ml.) can be obtained for amines with basic dissociation constants down to  $10^{-11}$ .

The pH values read off the meter have no absolute meaning when titrating in the glycol-isopropanol solvent; however, the changes in "apparent pH" are the most important factors in a titration, and these changes are accentuated in this medium to give the more accurate and precise titration.

### TITRATION IN GLACIAL ACETIC ACID <sup>42</sup>

In glacial acetic acid the titration curves are so accentuated—they are even sharper than in the glycol-isopropanol—that even good indicator end points can be obtained.

**Reagents.** Perchloric Acid, 0.1 *N*.—About 8.5 ml. of 70% perchloric acid are dissolved in 1 liter of glacial acetic acid. Add 15 ml. of acetic anhydride *cautiously* in small portions, and allow to stand overnight.

**Sodium Acetate Solution, 0.1 *N*.**—This is used to standardize the perchloric acid. Dissolve a weighed portion (about 0.53 g.) of dried sodium carbonate in enough acetic acid to make 100 ml. of solution. Potassium acid phthalate makes a very good and also convenient standard.

**Methyl Violet Indicator or Naphthol Benzein.**—0.25% solution in acetic acid.

**Procedure.**—The regular acid-base type titration is the procedure used here except that 25 to 50 ml. of glacial acetic acid is used as a solvent. The methyl violet indicator changes from the violet to a green, and the naphthol benzein goes from a

<sup>41</sup> Method of Palit, S., *Anal. Chem.*, 18, 246-251, 1946, as described by Siggia, S., *Quantitative Organic Analysis Via Functional Groups*, 2nd Ed., John Wiley and Sons, Inc., New York, pp. 104, 106, 1954.

<sup>42</sup> Method of Iritz, J. J., as described by Siggia, S., *op. cit.*, p. 103. Reprinted with permission of the copyright owner.

yellow to a green. Either indicator can be used. This solvent can be used for a potentiometric titration, using the standard pH meter with glass and calomel electrodes. Another set of electrodes can be used for this system, namely, the glass electrode as indicator electrode and a silver wire with a thin coating of silver chloride as the reference electrode.

The procedure is generally applicable to weak bases with dissociation constants down to  $10^{-10}$ . The end points obtained in acetic acid are generally sharper than those obtained in glycol-isopropanol, and accuracy and precision of  $\pm 0.3\%$  can easily be obtained.

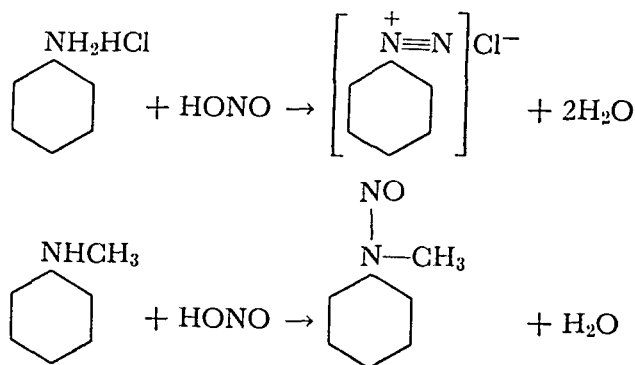
### TITRATION IN ACETONE <sup>43</sup>

Acetone can also be used as a solvent for titrating amines with a high degree of accuracy and with sharp end points for the weak bases. A solution of 0.1 *N* hydrochloric acid in glycol-isopropanol or a 0.1 *N* solution of *p*-toluenesulfonic acid in an alcohol can be used as titrating solution. The standard glass and calomel electrodes can be used for potentiometric titration.

### GENERAL METHODS IN DETERMINING AROMATIC AMINES BY DIAZOTIZATION AND NITROSATION <sup>44</sup>

No specific reference can be given for any general method of employing nitrous acid. The following procedure is a conglomeration of many known procedures.

The procedure will mainly determine primary and secondary amino groups.



#### Reagents.—

Sodium Nitrite.—1 *N*, 0.5 *N*, 0.1 *N*.

Starch-Iodide Paper.

Concentrated Hydrochloric Acid.

Glacial Acetic Acid.

Potassium Bromide Solution, 25%.

**Procedure.**—A sample of amine large enough to give a 20-ml. titration with nitrite of a certain strength is weighed into a 1-liter beaker and dissolved in about 500 ml. of water, 30 ml. of concentrated hydrochloric acid, and 25 or 50 ml. of 25% potassium bromide. (The amount of potassium bromide used depends on

<sup>43</sup> Siggia, S., *Quantitative Organic Analysis Via Functional Groups*, 2nd Ed., John Wiley and Sons, Inc., New York, pp. 105, 106, 1954.

<sup>44</sup> Siggia, S., *Quantitative Organic Analysis Via Functional Groups*, 2nd Ed., John Wiley and Sons, Inc., New York, pp. 108–111, 1954. Reprinted with permission of the copyright owners.

the ease of nitrosation of the amine.) Potassium bromide can be eliminated if the amine reacts rapidly. If the sample is not soluble in dilute acid, the sample can be dissolved in a few milliliters of glacial acetic acid and then the water and hydrochloric acid are added. The amine, in such cases, generally remains in solution.

The required strength of sodium nitrite depends on several factors: ease of nitrosation, clarity of end point, instability of the nitrous acid. The 1 *N* sodium nitrite will give a better end point, but the danger of losing nitrous acid is much greater since more is formed on each addition than is formed with the more dilute sodium nitrite. When the more dilute sodium nitrite is used, a poorer end point results, but the chances of loss of nitrous acid are lower.

The beaker containing the sample is immersed to within an inch of the rim in

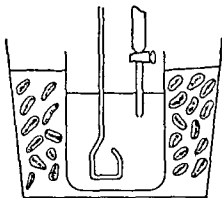


FIG 19-6. Apparatus for Determining Aromatic Amines by Diazotization and Nitrosation.

chopped ice and water until the temperature is about 5°C. This is to lower chances for loss of nitrous acid. Then, with the tip of the buret well under the surface of the solution (see Fig. 19-6), the nitrite standard solution is added at a rate depending on how rapidly the amine consumes the nitrous acid. There should never be a large excess of nitrite present, since this causes loss of nitrous acid. At first, the nitrite should be added in small increments and the solution tested by dipping into the solution a strip of starch-iodide paper; the paper turns the blue-black color of iodine in starch if nitrous acid is present. If the amine consumes the nitrous acid rapidly, the nitrite can be added more rapidly. If the amine nitrosates slowly, the nitrite is added

more slowly. The purpose of the potassium bromide is to catalyze the nitrosation; it should be added whenever the nitrite is consumed too slowly. If the amine nitrosates too slowly, the end point is very hard to detect. The nitrite is added in smaller increments as the end point is approached. This decreases the chance of overtitration.

The end point is the point at which the blue-black color is produced on the starch-iodide paper when the solution has stood for quite a time after the addition of nitrite. As the end point is approached the nitrite will be consumed more slowly so that a sufficient length of time (depending on the rate at which the particular amine nitrosates) should be allowed before testing for the end point. An excess of nitrite gives the blue-black color on the paper immediately on immersion in the solution. In some cases, the starch-iodide paper, on being dipped into the solution, does not darken immediately but darkens slowly on exposure to air. This should not be construed as indicating excess nitrite since the nitrite produces the color immediately. Colored amines and precipitates will hamper the viewing of any color on the paper. However, the presence of excess nitrite still can be shown by the solution that diffuses up the indicator paper, showing a blue-black portion above the mark which indicates the depth of the immersion of the paper in the solution.

The sodium nitrite is standardized by reaction with sulfanilic acid, which can be purchased in a pure state. The procedure is that described above.

## Calculations.—

$$\frac{\text{Ml. nitrite} \times N \text{ NO}_2^- \times \text{mol. wt. compound} \times 100}{\text{Grams sample} \times 1000 \times n} = \% \text{ compound based on diazotization or nitrosation}$$

$n$  = number of amino groups per molecule

**Discussion.**—Interfering substances consist mainly of compounds which are *readily* reduced by nitrous acid and also compounds which contain active methylene groups. The compounds with active methylene groups will nitrosate and can be determined by this procedure. The pyrazolones are such compounds.

### METHOD FOR DETERMINING MIXTURES OF PRIMARY, SECONDARY, AND TERTIARY AMINES<sup>45</sup>

**Reagents.** Ethylene Glycol-Isopropanol Mixture, 1:1.

**Hydrochloric Acid.**—Standard 1 *N*, in ethylene glycol-isopropanol mixture: 96 ml. of concentrated hydrochloric acid are diluted to 1 liter with 1:1 ethylene glycol-isopropanol.

**Acetic Anhydride**, c.p.

**Salicylaldehyde** (from bisulfite addition compound).

**Procedure A: Total Amines.**—A sample containing approximately 0.02 mole of total amines is accurately weighed in a weighing bottle. The contents of the weighing bottle are washed into a 150-ml. beaker with 1:1 ethylene glycol-isopropanol mixture. Ethylene glycol-isopropanol mixture is added until the volume is approximately 50 ml. A pH meter is used to indicate the apparent pH after each addition of acid as the sample is titrated with 1 *N* hydrochloric acid prepared in the ethylene glycol-isopropanol mixture. The neutralization point is determined by plotting the apparent pH against milliliters of acid.

$$\frac{\text{Ml. of HCl} \times N}{\text{Grams sample} \times 1000} = \text{moles total amines/gram sample}$$

**Procedure B: Secondary Plus Tertiary Amines.**—A sample containing approximately 0.02 mole total of secondary and tertiary amines is accurately weighed in a weighing bottle. The contents of the weighing bottle are washed into a 150-ml. beaker with 1:1 ethylene glycol-isopropanol mixture. Ethylene glycol-isopropanol mixture is added until the volume is approximately 50 ml. Five milliliters of salicylaldehyde are added (more should be used if the amount of primary amine is larger than 0.035 mole). The mixture is stirred thoroughly and allowed to stand at room temperature for one-half hour. A pH meter is used to indicate the apparent pH after each addition of acid as the sample is titrated with 1 *N* hydrochloric acid prepared in the ethylene glycol-isopropanol mixture. The neutralization point is determined by plotting apparent pH against milliliters of acid.

$$\frac{\text{Ml. HCl} \times N}{\text{Grams sample} \times 1000} = \text{moles secondary plus tertiary amine/gram sample}$$

<sup>45</sup> Method of Siggia, S., Hanna, J. G., and Kervenski, I. R., *Anal. Chem.*, **22**, 1295, 1950. Copyright 1950 by the American Chemical Society and reprinted with permission of the copyright owners.

In the case of the aliphatic amines, two breaks are usually obtained in the titration curve after the addition of the salicylaldehyde. This is due to the fact that the Schiff bases of the aliphatic amines still have a noticeable basicity although it is not so great as that of the original primary amine or that of the secondary and tertiary amines. The first break in the curve, therefore, is the secondary plus the tertiary amine content of the sample. The difference between the first and second breaks represents the primary amine content of the sample.

**Procedure C: Tertiary Amines.**—A sample that contains approximately 0.02 mole of tertiary amine is accurately weighed in a 20- by 150-mm. test tube and is cooled by placing in a beaker of ice. Ten milliliters of acetic anhydride are added slowly while the test tube is swirled. The test tube and contents are allowed to stand 15 minutes at room temperature. The contents are quantitatively transferred from the test tube into a 150-ml. beaker by washing with 1:1 ethylene glycol-isopropanol mixture.

Ethylene glycol-isopropanol mixture is added until the volume is approximately 50 ml. A pH meter is used to indicate the apparent pH after each addition of acid as the sample is titrated with 1 *N* hydrochloric acid prepared in the ethylene glycol-isopropanol mixture. The neutralization point is determined by plotting the apparent pH against milliliters of acid.

$$\frac{\text{Ml. of HCl} \times N}{\text{Grams sample} \times 1000} = \text{moles tertiary amines/gram sample}$$

#### Calculations.—

##### Primary Amine

$$\frac{\text{Moles total amine}}{\text{Gram}} - \frac{\text{moles secondary} + \text{tertiary amine}}{\text{gram}} = \frac{\text{moles primary amine}}{\text{gram}}$$

$$\frac{\text{Moles primary amine}}{\text{Gram}} \times \text{mol. wt. primary amine} \times 100 = \% \text{ primary amine}$$

##### Secondary Amine

$$\begin{aligned} \frac{\text{Moles secondary amine} + \text{tertiary amine}}{\text{Gram}} - \frac{\text{moles tertiary amine}}{\text{gram}} \\ = \frac{\text{moles secondary amine}}{\text{gram}} \end{aligned}$$

$$\frac{\text{Moles secondary amine}}{\text{Gram}} \times \text{mol. wt. secondary amine} \times 100 = \% \text{ secondary amine}$$

##### Tertiary Amine

$$\frac{\text{Moles tertiary amine}}{\text{Gram}} \times \text{mol. wt. tertiary amine} \times 100 = \% \text{ tertiary amine}$$

## HYDRAZINE COMPOUNDS

METHOD FOR DETERMINING WATER SOLUBLE,  
ALIPHATIC HYDRAZINES <sup>46</sup>

*Reagents.* Iodine.—Standard 0.1 *N*.

Sodium Bicarbonate.

Starch Indicator.

*Procedure.*—About 0.0005 to 0.0001 mole of hydrazine is dissolved in about 20 to 50 ml. of water. About 1 g. of sodium bicarbonate is added, and the solution is titrated with 0.1 *N* iodine, starch being used as an indicator.

*Calculation.*—

$$\frac{\text{Ml. I}_2 \times N \text{ I}_2 \times \text{mol. wt. hydrazine} \times 100}{\text{Grams sample} \times 4000} = \% \text{ hydrazine}$$

GENERAL METHOD FOR DETERMINING HYDRAZINES BY  
OXIDATION WITH CUPRIC ION <sup>47</sup>

This method applies quite generally to aromatic hydrazines, substituted and unsubstituted. It also applies to a good number of aliphatic substituted and unsubstituted hydrazines.

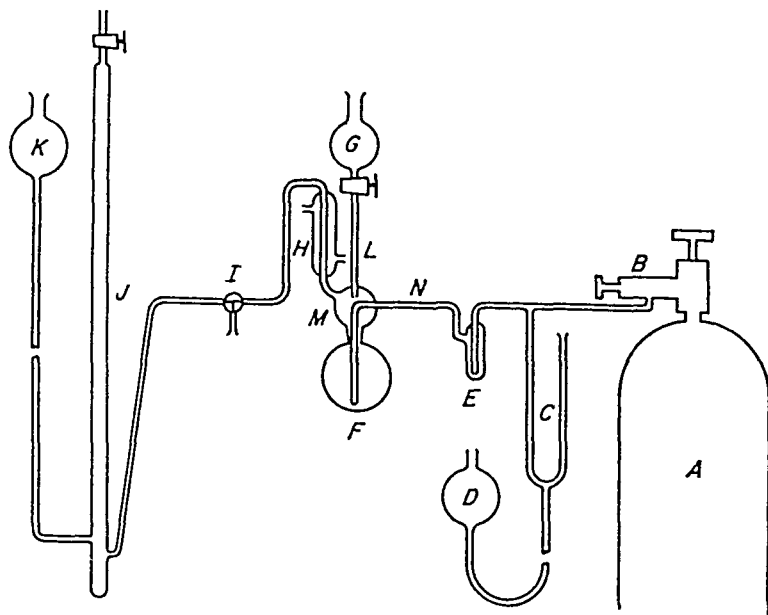


FIG. 19-7. Apparatus for Determining Hydrazines by Oxidation with Cupric Ion.

*Apparatus.*—The apparatus, shown in Fig. 19-7, consists essentially of a reaction flask, *F*, in which the nitrogen is liberated, a Lunge nitrometer, *J*, in which the

<sup>46</sup> Method of Rosin, J., Reagent Chemicals and Standards, D. Van Nostrand Co., Inc., Princeton, N. J., p. 194, 1939.

<sup>47</sup> Siggia, S., and Lohr, L. J., Anal. Chem., 21, 1202, 1949. Copyright 1949 by the American Chemical Society and reprinted with permission of the copyright owners.

liberated nitrogen is measured over 50% potassium hydroxide, and a cylinder of purified carbon dioxide, *A*, which is used to displace the air from the apparatus prior to an analysis and to sweep the liberated nitrogen into the nitrometer.

The 100-ml. reaction flask, *F*, is attached to the apparatus by a standard taper 24/40 joint. The reagents are introduced through the separatory funnel, *G*, and the delivery tube, *L*, which has a maximum diameter of 3 or 4 mm. and a constriction at the bottom to prevent displacement of the liquid during decomposition of the sample. The reflux condenser, *H*, which is sealed to *M*, has an internal diameter of 12 mm. and allows vigorous refluxing of the reactants.

The carbon dioxide rate is controlled by the needle valve, *B*, and is estimated by the bubble counter, *E*, which is filled with an inert liquid such as butyl phthalate.

Other essential parts of the apparatus are the safety manometer, *C*, the leveling bulbs, *D* and *K*, and the three-way stopcock, *I*, which permits bypassing the nitrometer.

Commercial tank carbon dioxide is purified prior to use by venting rapidly about 50% of the carbon dioxide from the cylinder. A cylinder of carbon dioxide purified by this procedure contains a negligible impurity and contains sufficient carbon dioxide for several hundred analyses.

**Procedure.**—The apparatus is prepared for an analysis by completely displacing the air with carbon dioxide up to the reaction flask, *F*. The mercury in the safety tube, *C*, is lowered to a point slightly below the curved section of the manometer, so that carbon dioxide can be passed through the manometer to the atmosphere. After the air is completely displaced from the manometer, the leveling bulb, *D*, is raised until the mercury level is approximately halfway up the manometer. The carbon dioxide rate is then increased, and in several minutes the air will be completely displaced up to *F*. The delivery tube, *L*, is filled with water.

A sample that will give from 15 to 25 cc. of nitrogen is weighed into *F*, which is securely fastened to the apparatus by tension springs. Stopcock *I* is opened to the atmosphere, and carbon dioxide is rapidly passed through the apparatus until the air is completely displaced by carbon dioxide. This will acquire from 5 to 10 minutes. After displacing the air, the carbon dioxide rate is reduced to 1 to 2 bubbles per second. Stopcock *I* is closed so the carbon dioxide passes into the nitrometer, and after several minutes microbubbles are obtained. The air collected in the nitrometer is displaced, and the leveling bottle lowered until it is about level with the nitrometer inlet tube. Forty milliliters of saturated copper sulfate, 15 ml. of 95% sulfuric acid, and 10 ml. of distilled water are drawn into the reaction flask. The solution is boiled until the reaction is complete and microbubbles are obtained. The carbon dioxide rate can be increased after the reaction appears complete to speed up sweeping the liberated nitrogen into the nitrometer. A blank is then determined on an equal volume of copper sulfate, sulfuric acid, and water and is usually about 0.6 ml.

**Calculations.**—*A* = volume for nitrogen corrected for a blank for the carbon dioxide; *p* = barometric pressure corrected for vapor pressure of potassium hydroxide \* solution at temperature *T*.

\* See table under "Diazonium Salts."



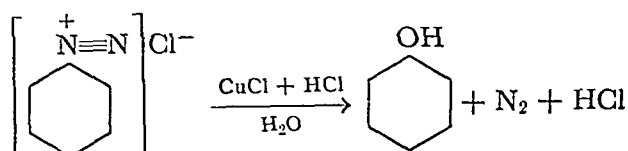
$$\frac{pA}{T + 273} = \frac{A'760}{273}$$

$$\frac{1}{22,400} = \frac{x}{A'} \quad (x = \text{moles of nitrogen collected})$$

$$\frac{x \times \text{mol. wt. hydrazine} \times 100}{\text{Grams of sample}} = \% \text{ hydrazine}$$

## DIAZONIUM SALTS

### GENERAL METHOD USING DECOMPOSITION AND MEASUREMENT OF THE NITROGEN LIBERATED <sup>48</sup>



*Apparatus (Fig. 19-8).—*

*A* = 25-ml. separatory funnel.

*B* = 100-ml. nitrometer containing 50% potassium hydroxide.

*C* = 10-mm. tubing.

*D* = 2-mm. capillary.

*G* = 5-in. condenser.

*H* = bubbler.

*I* = thermometer.

*J* = 150-ml. flask.

*Reagents.* Cuprous Chloride.

Concentrated Hydrochloric Acid.

*Procedure.*—In about 15 ml. of concentrated hydrochloric acid, 3 g. of cuprous chloride is dissolved and the resultant solution is placed in the separatory funnel, *A*. A sample containing about 0.001 mole of diazonium salt is weighed into the reaction flask. The flask is attached to the condenser, all joints being greased to prevent leakage. The nitrometer, *B*, contains potassium hydroxide solution (71.5 g. of potassium hydroxide per 100 ml. of water) and a layer of mercury at the bottom. The level of the mercury extends about ½ in. above the entrance tube. The function of the mercury is to prevent clogging of the capillary, *D*, with potassium carbonate. Carbon dioxide is passed through the apparatus to flush out the air; it is continuously passed through until the bubbles reach a minimum size in the nitrometer. These minute bubbles are indicative of the potassium hydroxide insoluble impurities contained in the carbon dioxide. A blank run should be made on each cylinder of carbon dioxide to correct the volume readings for each sample. The blank determination is made as follows: After all the air is swept out of the apparatus, the accumulated inert gas is removed from the nitrometer and

<sup>48</sup> Siggia, S., *Quantitative Organic Analysis Via Functional Groups*, 2nd Ed., John Wiley and Sons, Inc., New York, pp. 124–127, 1954. Reprinted with permission of the copyright owners.

the number of bubbles of carbon dioxide per minute (2 bubbles per second is a convenient rate) is counted and the time is noted. Every 15 minutes the nitrometer is read to obtain the volume of inert gas collected in the period. This is done over a period of 2 to 3 hours. The average is taken for the volume of inert gas collected per 15 minutes at that particular rate of flow. When a sample is analyzed, the carbon dioxide is fed in at the same rate as in the case of the blank. The time required for the sample to react completely is noted, the carbon dioxide

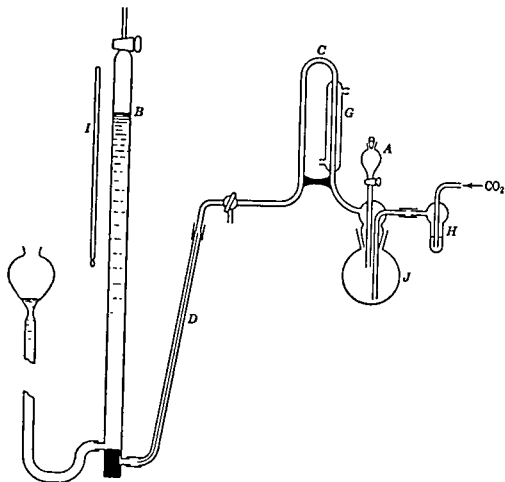


FIG. 19-8. Diazo Nitrogen Apparatus.

blank is computed for that length of time and is subtracted from the volume recorded in the nitrometer. This correction is usually small but it is significant. Large blanks resulting from impure carbon dioxide decrease the accuracy of the results.

In an actual determination, the air is swept out of the apparatus as previously described. The inert gas is removed from the nitrometer and the solution of cuprous chloride in hydrochloric acid is allowed to flow from the separatory funnel, *A*, into the reaction flask, *J*, which contains the sample, and the time is noted. The cuprous chloride is followed by 50 to 75 ml. of water, no air being allowed to enter the apparatus. The reaction flask is heated to boiling and kept at that temperature until the reaction is complete, as indicated by the bubbles in the nitrometer reaching their minimum size. The heat is shut off, and the apparatus is al-

lowed to stand for 5 to 10 minutes to reach temperature equilibrium. The carbon dioxide flow is continued throughout this period of standing. The volume of gas collected is read, the leveling bulb on the nitrometer being used to set the pressure of the gas in the nitrometer equal to atmospheric pressure. The temperature is read on thermometer, *I*, and the barometric pressure and time are noted. The volume of gas collected is corrected for the blank determination made on the carbon dioxide, the time required for the reaction being taken into account. The volume is also corrected for the vapor pressure of the potassium hydroxide solution.

VAPOR PRESSURE OF POTASSIUM HYDROXIDE SOLUTIONS CONTAINING 71.5 GRAMS OF POTASSIUM HYDROXIDE PER 100 GRAMS OF WATER

(International Critical Tables)

°C.	mm. Hg
15.....	4.1
20.....	5.6
25.....	7.4
30.....	9.6
35.....	12.7

Calculations.—

*A* = volume of gas, corrected for carbon dioxide blank

*P* = atmospheric pressure — vapor pressure of the 50% potassium hydroxide solution

*T* = temperature recorded at the end of analysis

$$\frac{AP}{T + 273} = \frac{A_1 760}{273}$$

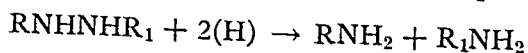
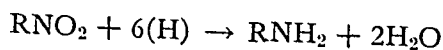
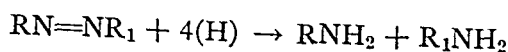
*A*<sub>1</sub> = volume calculated to N.T.P.

$$\frac{1}{22,400} = \frac{x}{A_1} \quad (x = \text{moles of nitrogen collected})$$

$$\frac{x \times \text{mol. wt. diazonium compound} \times 100}{\text{Grams sample}} = \% \text{ diazonium compound}$$

AZO, HYDRAZO, AND NITRO COMPOUNDS (—N=N—,  
—NHNH—, AND —NO<sub>2</sub>)

GENERAL METHOD BY REDUCTION WITH  
TITANOUS CHLORIDE <sup>49</sup>



<sup>49</sup> Siggia, S., Quantitative Organic Analysis Via Functional Groups, 2nd Ed., John Wiley and Sons, Inc., New York, pp. 128–130, 1954. Reprinted with permission of the copyright owner.

This procedure is readily adaptable to reduction of azo, hydrazo, and nitro groups. Indications are that this procedure may also be applicable to the reduction of diazonium compounds. Titanous ion is a strong reducing agent, and this is one of its drawbacks; atmospheric oxygen will oxidize it. The reagent must be stored under an inert atmosphere, and the reduction must be carried out under nitrogen. With proper precautions for elimination of oxygen, the procedure can be used with good accuracy and precision.

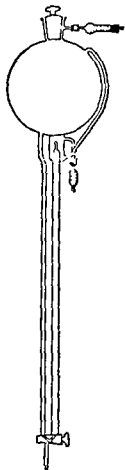


FIG. 19-9. Storage Buret for Titanous Chloride.

**Reagents. Titanous Chloride.**—One liter of water containing 100 ml. of concentrated hydrochloric acid is boiled to remove dissolved oxygen. This solution is cooled under nitrogen, and to it is added 560 ml. of 20% titanous chloride ( $\text{TiCl}_3$  is sold in 20% solution). The solution is diluted to 2 liters with freshly boiled and cooled distilled water. The solution is stored under hydrogen or oxygen-free nitrogen in an apparatus as depicted in Fig. 19-9.

**Ammonium Thiocyanate.**—10% solution.

**Ferric Ammonium Sulfate Solution.**—In 600 ml. of water 282 g. of ferrous ammonium sulfate is dissolved, and 50 ml. of concentrated sulfuric acid is added. To the still warm solution, 80 to 100 ml. of Perhydrol (30% hydrogen peroxide) is added slowly, with stirring. The excess peroxide is boiled off, and the solution is cooled and diluted to 4 liters. To standardize the ferric ammonium sulfate solution 20 ml. of the solution is placed in a 250-ml. iodine flask together with 4 ml. of 4 *N* hydrochloric acid. Then 2 g. of potassium iodide is added, and the solution is allowed to stand for 5 minutes. The liberated iodine is titrated with 0.1 *N* sodium thiosulfate to the starch end point.

**Apparatus.**—Storage buret for titanous chloride (Fig. 19-9).

The buret, as indicated in Fig. 19-9, is used for Karl Fischer reagent. This reagent must be protected from water vapor so that ascarite tubes are shown in the diagram. Titanous chloride solution must be protected against oxygen so that the ascarite tubes do not apply in this case. For titanous chloride solution a hydrogen generator (a Kipp generator) is attached to the vent from the storage bulb. In this manner, a continuous hydrogen atmosphere is maintained above the solution.

Attached to the vent of the measuring buret section of the apparatus is a small stopcock.

When the apparatus is charged with titanous chloride solution, the atmosphere above the solution is purged of air by turning the buret stopcock so that the measuring buret is open to the atmosphere at the tip. The hydrogen from the generator will then flow through the bypass tube from the reservoir, to the buret, and on to the outside through the buret tip. This operation will purge the buret as well as the atmosphere above the titanous chloride solution. In filling the measuring buret, the stopcock is turned to connect the buret to the reservoir. Then the stopcock on the vent of the buret is opened, and the buret will fill with reagent. The reagent entering the buret will force out the hydrogen through the stopcock at the vent. As soon as the buret is filled to the desired level, both the stopcock at the

vent and at the tip of the buret are closed. To introduce the reagent to the reaction vessel, the stopcock at the buret tip is opened to the reaction vessel containing the sample (through which oxygen-free nitrogen is bubbling). The hydrogen pressure in the apparatus will cause the solution to flow out of the buret.

Reaction flask (Fig. 19-10).

**Procedure.**—About 0.005 equivalent of sample is placed in a 500-ml. Erlenmeyer flask and dissolved in water or in glacial acetic acid if the sample is water insoluble. The flask is then equipped as shown in Fig. 19-10 to keep the reaction under nitrogen. Oxygen-free nitrogen is passed through the sample for 5 to 10 minutes. Next 25 ml. of titanous chloride solution, 30 ml. of concentrated hydrochloric acid, and 2 ml. of hydrofluoric acid are added. The solution is boiled for 5 minutes (a longer time may be needed for some samples). A condenser should be attached to the reaction flask for volatile samples. With the nitrogen still bubbling through the solution, the flask is cooled in ice, and 10 ml. of 10% ammonium thiocyanate are added. The solution is titrated with the ferric ammonium sulfate solution to a red end point, while the nitrogen is kept bubbling through the solution.

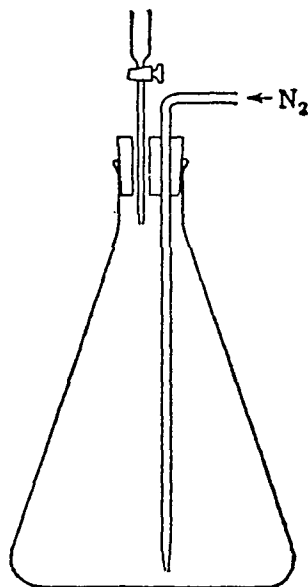


FIG. 19-10. Reaction Flask.

A blank should be run on the titanous chloride for each set of reductions. The same solvent should be used for the blank as is used for the sample.

**Calculations.**—

$$\frac{(\text{ml. F.A.S. blank} - \text{ml. F.A.S. sample}) \times N_{\text{F.A.S.}} \times \text{mol. wt. compound} \times 100}{\text{Grams sample} \times 1000 \times A} = \% \text{ compound}$$

$A$  = number of hydrogen atoms consumed per molecule of compound

**Discussion.**—Oxygen is the most troublesome interference in this procedure; however, any reducible substance will usually interfere. Ethylenic or acetylenic compounds generally will not be reduced by titanous chloride.

## MERCAPTANS

### GENERAL METHOD BY TITRATION WITH SILVER ION

#### INDICATOR METHOD <sup>50</sup>

**Reagents.** Silver Nitrate Solution.—Standard 0.005 *N*.

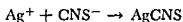
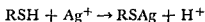
Ammonium Thiocyanate Solution.—0.005 *N*, standardized against the silver nitrate solution.

<sup>50</sup> Method of Malisof and Anding, *Ind. and Eng. Chem., Anal. Ed.*, 7, 86, 1935, as described by dal Nogare, S., in *Organic Analysis*, Vol. I, Interscience Publishers, Inc., New York, pp. 333–334, 1953 (edited by Mitchell, J., Jr., et al.). Reprinted with permission of the copyright owner.

**Ferric Alum Indicator.**—Approximately 40 g. of ferric alum is dissolved in 100 ml. of 1 *N* nitric acid. The solution is boiled to remove nitrogen oxides, cooled, and diluted with three volumes of distilled water.

**Procedure.**—A solution of 1 to 2 milliequivalents of mercaptan in 100 ml. of benzene, naphtha, octane, or heptane is prepared from an accurately weighed sample. Exactly 10 ml. of the sample solution are transferred to a 250-ml. Erlenmeyer flask followed by 10 ml. of anhydrous methanol. Approximately 45 ml. of 0.005 *N* silver nitrate solution are added from a buret to the sample solution which is continuously agitated. Two ml. of ferric alum indicator are added, and the solution is titrated with 0.005 *N* ammonium thiocyanate solution until a faint pink end point is reached. The solution should also be continuously agitated during the course of this titration. The pink color is discharged by adding standard silver nitrate in slight excess and the pink end point is restored by titrating again with the standard thiocyanate solution. Continuous agitation during titration is extremely important.

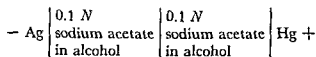
**Calculation.**—Calculate the mercaptan content of the sample from the stoichiometry of the following equations:



**Discussion.**—This procedure is not subject to interference from sulfides, disulfides, or free sulfur. However, solutions of mercaptans prepared in the recommended solvents are oxidized to disulfides on exposure to light. This effect is greater for aromatic than for aliphatic mercaptans and occurs in benzene solutions more readily than in octane, naphtha, or heptane. It is recommended that sample solutions be used as soon after preparation as possible to reduce to a minimum the error resulting from this cause.

#### POTENTIOMETRIC TITRATION WITH SILVER NITRATE<sup>51</sup>

The potentiometric determination of mercaptans was first described in a publication by Tamele and Ryland and is based on the titration of an ethanolic solution of the mercaptans with a standard isopropyl alcohol solution of silver nitrate. For detecting the end point of this titration, a cell consisting of:



which has an e.m.f. of  $-0.070$  volt, was employed. The electrolyte bridge is also filled with 0.1 *N* sodium acetate. Addition of the alcoholic mercaptan solution to the silver cell increases the e.m.f. to about  $-0.38$  volt which slowly decreases as the end point is neared. At the end point, a steep inflection to an e.m.f. of  $+0.30$  volt is observed, with the actual end point occurring at about  $-0.10$  volt. With careful work, the precision of the potentiometric end point is  $\pm 1.0\%$  which is near the limit of  $\pm 0.8\%$  to be expected from an end point which can be detected

<sup>51</sup> Method of Tamele and Ryland, *Ind. and Eng. Chem., Anal. Ed.*, 8, 16, 1936, as described by dal Nogare, S., in *Organic Analysis*, Interscience Publishers, Inc., New York, pp. 335–337, 1953. Reprinted with permission of the copyright owner.

graphically to  $\pm 0.02$  ml. This precision is based on the use of 0.01 *N* silver nitrate and an approximately 0.0025 *M* mercaptan solution. The high absolute accuracy of the potentiometric method was demonstrated by the titration of high-purity samples with excellent recovery even with a number of serial dilutions. An estimate of the solubility of the common mercaptides can be obtained from the fact that the end point at or near  $-0.10$  volt is slightly less than that obtained on precipitating silver iodide. For analytical purposes the slight variation in solubility among individual mercaptans is of no consequence although, by suitable modification, this technique may be used to calculate solubility products. Because of the insolubility of silver mercaptides, this method of analysis is not subject to interference from compounds which react with silver nitrate as long as the reaction products have an appreciably greater solubility than the mercaptides. No difficulty is encountered with highly colored samples and little if any difficulty is encountered with unsaturated compounds. The use of alcoholic solutions eliminates the problem of silver ion adsorption. The use of sodium acetate buffer prevents loss of mercaptan by volatilization and neutralizes the hydrogen ion formed during the titration. Hydrogen sulfide is an interference in this method.

## ORGANIC DISULFIDES

### GENERAL METHOD BY REDUCTION AND TITRATION OF THE MERCAPTAN FORMED <sup>52</sup>

**Reagents.** Sodium Borohydride.—Two grams dissolved in 100 ml. of diethylene glycol dimethyl ether (Ansul Chemical Company, Marinette, Wis.).

Anhydrous Aluminum Chloride.

Sodium Hydroxide, 1 *N*.

Sodium Hydroxide, 6 *N*.

Nitric Acid, 3 *M*.

Concentrated Ammonium Hydroxide.

Silver Nitrate.—Standard 0.1 *N*.

**Procedure.**—A sample containing approximately 0.001 mole of disulfide is accurately weighed and placed in a 150-ml. round-bottomed flask containing 15 ml. of sodium borohydride solution and approximately 0.5 g. of aluminum chloride.

**Caution.**  $\text{AlCl}_3$  occasionally reacts violently in contact with reagent. It is best to dissolve the  $\text{AlCl}_3$  in 5 ml. of diethylene glycol dimethyl ether before mixing. The flask is immediately attached to a coil condenser 40 cm. long, and the reduction is allowed to proceed at room temperature for 0.5 hour. The order of addition of reagents and sample to the flask is unimportant except in the case of methyl disulfide. When the sodium borohydride solution and the aluminum chloride are mixed, a rapid reaction takes place, and methyl disulfide is lost if it is added to the solution before the aluminum chloride. In the determination of methyl disulfide the sodium borohydride solution and the aluminum chloride are mixed (see *Caution* above) and allowed to stand in an ice bath for a few minutes while the sample is being weighed.

After reduction is complete, the flask is submerged in an ice bath, and 5 ml. of

<sup>52</sup> Method of Siggia, S., and Stahl, C. R., *Anal. Chem.*, **29**, 154–155, 1957. Copyright 1957 by the American Chemical Society and reprinted with permission of the copyright owners.

1 *N* sodium hydroxide are added through the condenser. The sodium hydroxide is added a few drops at a time until the initial vigorous reaction subsides, and then the remainder is added, and the condenser is rinsed with a few milliliters of distilled water. The solution is allowed to stand for 2 or 3 minutes and 10 ml. of 3 *M* nitric acid are added. The ice bath is removed, and 10 ml. of 6 *N* sodium hydroxide are added after about 2 minutes. In determining methyl disulfide it is better to allow the solution to stand 5 minutes in the ice bath after adding the nitric acid and to add the sodium hydroxide before removing the ice bath.

The condenser is rinsed with a few milliliters of distilled water, and the flask is removed. The contents of the flask are rinsed into a 400-ml. beaker, and 10 ml. of concentrated ammonium hydroxide are added. Using a pH meter equipped with silver and calomel electrodes, the solution is titrated potentiometrically with standard 0.1 *N* silver nitrate solution. The break occurs between approximately -325 and -175 mv., although it varies somewhat for the different mercaptans being titrated. Per cent disulfide is calculated in the following manner:

$$\% \text{ Disulfide} = \frac{\text{ml.} \times N \text{ of AgNO}_3 \times \text{mol. wt.} \times 100}{\text{wt. of sample} \times 2000}$$

## SULFONAMIDES

### GENERAL METHOD BY TITRATING AS ACIDS<sup>53</sup>

**Reagents.** Butylamine.—Commercially available material is used without purification.

Dimethylformamide.—Commercially available material is used without purification.

*p*-Nitrobenzeneazoresorcinol (azo violet).—Saturated solution in benzene.

Thymol Blue.—0.3 g. dissolved in 100 ml. of methanol.

Sodium Methoxide, 0.1 *N*.—About 6 g. of sodium is washed with methanol (absolute) and immediately dissolved in 100 ml. of methanol; the solution is protected from carbon dioxide during preparation and is cooled in cold water if the reaction becomes too vigorous. After the sodium has dissolved, an additional 150 ml. of methanol and 1500 ml. of benzene are added. The reagent is stored in borosilicate glass and protected from carbon dioxide; the solution is reasonably stable but should be restandardized every few days by titrating weighed amounts of pure benzoic acid dissolved in dimethylformamide to the thymol blue end point. About 25 ml. of solvent is used for each 100 mg. of benzoic acid taken.

**Procedure.**—A sample of the sulfonamide of suitable size is weighed into a 50-ml. beaker and dissolved in 10 to 20 ml. of dimethylformamide or butylamine and the indicator is added. The solvent should be neutralized to the indicator end point prior to used.

The beaker is covered with a cardboard, or other suitable cover, provided with an opening for the buret tip and the solution is titrated to the first appearance of a clear blue color. The solution is stirred continuously during the titration by means of a magnetic stirrer.

<sup>53</sup> Method of Fritz, J. S., and Keen, R. T., *Anal. Chem.*, 24, 308, 1952, as described by dal Nogare, S., in *Organic Analysis*, Vol. I, Interscience Publishers, Inc., New York, pp. 386-387, 1953 (edited by Mitchell, J., Jr., et al.). Reprinted with permission of the copy-right owners.



Calculation of the sulfonamide content of the sample is made in the same way as for ordinary acid-base analyses. For compounds containing one— $\text{SO}_2\text{NH}$ —group the equivalent weight is taken as the molecular weight.

**Discussion.**—The azo violet indicator is used when the titrations are carried out in butylamine, and the thymol blue indicator is employed when dimethylformamide is used as the solvent. Consideration of the structure of the compound to be analyzed and its acidity determine whether butylamine or dimethylformamide is to be used as the solvent. Sulfonamides which contain an *N*-alkyl group have a low acidity and give poor end points even in butylamine. Some improvement in the end point will probably be effected by the use of 95 to 100% ethylenediamine. If no substituent is present or if a naphthyl group is attached to the nitrogen, butylamine is very satisfactory. If the compound contains an *N*-phenyl or *N*-pyridyl group, dimethylformamide is used as the solvent. Phenolic groups cause no interference in dimethylformamide but have a sufficiently high relative acidity in butylamine to alter the azo violet end point.

By appropriate changes in solvents to take advantage of a large difference in acidity, it is possible to determine the components of certain simple mixtures of sulfonamides. Thus, a mixture of sulfanilamide and sulfathiazole can be analyzed by titrating the sulfathiazole in dimethylformamide and thymol blue followed by a second titration of another sample, using butylamine and azo violet for the total sulfonamide content.

## OXIRANE OXYGEN COMPOUNDS

### GENERAL METHOD USING HYDROCHLORINATION

**In a Pyridine Solvent.**<sup>54</sup>—The hydrochlorination reagent, a 0.2 *N* solution of hydrochloric acid in pyridine, is prepared by cautiously pipetting 17 ml. of c. p. concentrated hydrochloric acid into 1 liter of c. p. pyridine and mixing thoroughly. Twenty-five milliliters of the pyridine hydrochlorination reagent is pipetted into a 250-ml. flask, equipped with a standard taper joint. A weighed amount of sample, containing from 0.002 to 0.003 equivalent of  $\alpha$ -epoxide, is added and dissolved by heating the mixture at about 40°C. After dissolution is complete, the mixture is refluxed, under a condenser, on a hot plate for 20 minutes. The flask and contents are cooled, 6 ml. of distilled water are added, together with 0.2 ml. of phenolphthalein indicator solution, and the titration made with standard 0.1 *N* methanolic sodium hydroxide solution to a definite pink color.

**In an Aqueous Magnesium Chloride System.**<sup>54</sup>—The hydrochlorination reagent is a saturated magnesium chloride solution, which is 0.1 *N* in hydrochloric acid. It is prepared by shaking 1000 g. of c. p. magnesium chloride hexahydrate with 300 ml. of distilled water and adding 8.0 ml. of concentrated hydrochloric acid. The mixture is shaken at room temperature until saturated and allowed to settle for at least 2 hours. At the end of this time, the supernatant liquid is decanted through glass wool and stored in a glass-stoppered bottle. Fifty milliliters of the aqueous hydrochlorination reagent is pipetted into a 250-ml. glass-stoppered flask. Because of the viscosity of the reagent, a consistent drainage period should be maintained. A weighed amount of sample containing from 0.001 to 0.002 equivalent of  $\alpha$ -epoxide

<sup>54</sup> Jungnickel, J. L., Peters, E. D., Polgar, A., and Weiss, F. T., *Organic Analysis*, Vol. I, Interscience Publishers, Inc., New York, pp. 134–137, 1953. Reprinted with permission of the copyright owners.

is added, and the flask is shaken and allowed to stand 15 to 30 minutes. The stopper and neck of the flask are rinsed with not more than 20 ml. of distilled water. Several drops of a 0.1% methyl orange indicator solution are added and the mixture is titrated with standard 0.1 *N* aqueous sodium hydroxide solution.

**In Diethyl Ether.**—The hydrochlorination reagent is prepared by passing anhydrous hydrogen chloride into absolute ethyl ether until an approximately 0.2 *N* solution is obtained. A sample containing not more than 0.002 equivalent of  $\alpha$ -epoxide is weighed into a glass-stoppered flask. The sides of the flask are washed down with 5 ml. of absolute ethyl ether, and 25 ml. of the hydrochlorination reagent is pipetted into the flask, which is stoppered, mixed, and allowed to stand for 3 hours at room temperature. A few drops of phenolphthalein indicator solution and 50 ml. of 95% ethanol are added and the contents of the flask titrated with standard 0.1 *N* aqueous sodium hydroxide solution.

## ISOCYANATES AND ISOTHIOCYANATES

### GENERAL METHOD USING REACTION WITH BUTYL AMINE<sup>55</sup>

**Reagents. Butylamine Solution.**—Dilute 25 g. of mono-*n*-butylamine to 1 liter with dioxane, which has been dried over potassium hydroxide pellets.

**Sulfuric Acid.**—Standard 0.1 *N*.

**Procedure.**—A sample containing approximately 0.002 mole of isocyanate or isothiocyanate is weighed in a small glass-stoppered weighing bottle. Very volatile samples are weighed in sealed glass ampoules. The stopper from the weighing bottle is removed, and the weighing bottle containing the sample is placed in a 250-ml. Erlenmeyer flask. To the flask are added 20 ml. of the butylamine solution, and the flask is swirled to mix the reactants. Alkyl isocyanates and alkyl isothiocyanates are allowed to stand 45 minutes at room temperature for complete reaction. Aromatic compounds react more rapidly with the butylamine, and the reaction mixture can be titrated immediately after mixing the reactants. Then 25 ml. of distilled water are added, and the solution is titrated to the methyl red end point with 0.1 *N* sulfuric acid. A blank is run on 20 ml. of the butylamine solution. From the difference between the two titrations, the amount of isocyanate or isothiocyanate in the sample can be calculated.

<sup>55</sup> Siggia, S., and Hanna, J. G., *Anal. Chem.*, 20, 1084, 1948. Copyright 1948 by the American Chemical Society and reprinted with permission of the copyright owner.

## Chapter 20

# SOLUBILITY MEASUREMENTS

By William F. Linke

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Solubility determinations have become a routine procedure in the characterization and identification of new materials. Even such simple generalizations as "like dissolves like" are still useful in predicting solubilities in a qualitative way, but for most purposes a direct and accurate measurement of the solubility is required. This chapter is limited to solubility determinations made near atmospheric pressure and within 100°C. of room temperature. Measurements at extremes of temperature or pressure require elaborate apparatus and skill and are not included. References to other methods, to more complex systems, and to compilations of solubility data are given at the end of the chapter.

In the usual solubility determination, the experimental problems, in order of occurrence, are:

- (1) Maintaining constant temperature
- (2) Being sure that equilibrium (saturation) has been attained
- (3) Sampling
- (4) Identifying and/or analyzing the phases

Problems (1) and (3) are essentially mechanical; (2) and (4) often require some chemical ingenuity. A number of specialized techniques which can reduce the chance of error in these operations are described in the following sections.

### EXPRESSION OF RESULTS—UNITS AND METHODS

The simplest, and often the most accurate, method of expressing solubilities is in the units of the analytical method employed. Gravimetric analysis, such as in the evaporation of a solution to dryness, or in the weighing of a precipitate, leads directly to a weight-percentage expression; volumetric analysis yields the number of equivalents; etc. There can be little ambiguity when the data are left in the form in which they were obtained.

Care should be taken to define all terms precisely. For example, reporting solubilities as "moles per liter" immediately raises the questions: "per liter of solvent or of saturated solutions?", "moles of what formula weight?". When the data are expressed in theoretical form, as equations or as solubility parameters for example, it is highly desirable to state them also on a simple weight or molar basis. Even the conversion from a mole to a weight basis can be tedious, especially in systems of several components, and duplicate tabulations are often justified. The

## TEMPERATURE CONTROL

**Liquid Thermostats.**—Good temperature control is essential for all but the crudest measurements. The temperature must be held constant throughout the saturation, settling, and sampling steps, and care must be taken to avoid temperature changes caused by evaporation, introduction of pipets, or by chemical reactions (e.g., phase changes) within the system.

For work between 0° and 100°C. a thermostated water bath is usually most convenient, and can easily maintain temperature to  $\pm 0.1^\circ\text{C}$ ., and with care to  $\pm 0.01^\circ\text{C}$ . Above about 50°C. there is considerable steaming, however, and a thin layer of mineral oil is usually placed on the surface. Below 0° and above 100°C., water-glycol mixtures are useful. For higher temperatures, mineral oil or silicone oil baths can be used.

The thermostat is easily made from a large jar or tank (preferably insulated), fitted with a stirrer, thermometer, heater (and/or cooler), and a temperature regulator. The choice of instrument parts depends on the required precision, which in turn depends on the system being studied. For example, at 20°C., the solubility of  $\text{KNO}_3$  in water is 24.0% by weight, and changes by about 0.7% by weight per degree. In this system then, a precision of 0.1% in a solubility determination requires temperature control within  $\pm 0.03^\circ$ .

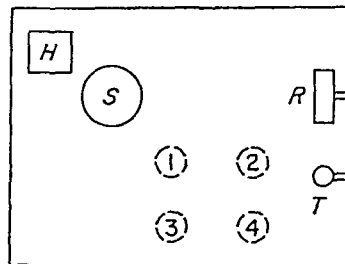


FIG. 20-1. Arrangement of Component Parts in a Thermostated Bath. Stirrer *S* is placed near heater *H* to diffuse the heat rapidly. Thermoregulator *R* and thermometer *T* are placed near samples 1, 2, 3, 4.

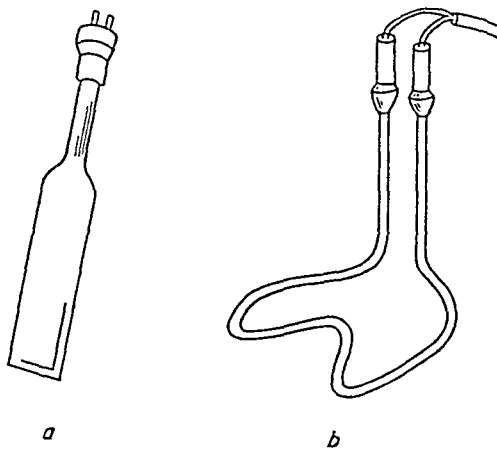


FIG. 20-2. *a*. Knife-Blade Heater. *b*. Flexible-Tube Heater to Spread Heat Over Bottom of Bath.

$$\frac{\pm 0.001 \times 24.0}{0.7} = \pm 0.03^\circ$$

Several points in obtaining good control should be noted:

1. The stirrer should provide turbulent mixing to produce the same temperature in all parts of the bath. It should be located near the heater in order to diffuse the heat rapidly and prevent local "hot spots."

2. The heater wattage is determined by the temperature to be maintained, and on the size and insulation of the bath. The heater size is a prime factor in temperature "cycling" above and below the desired point. Large heating elements that are alternately switched on and off take time to heat up and cool down. The best control is obtained when small heaters are switched on and off, and appropriately sized "constant" heaters are used to maintain the bath a few degrees below the desired temperature. Large heaters are also undesirable be-

cause of the excessive loading they impose upon thermoregulator components. Some difficulty is usually experienced in maintaining a bath near room temperature where the rate of cooling is slow and the temperature remains "high" for a large part of the cycle. The bath must then be cooled by a continuous drip of cold water (with overflow), or by a fan blowing across the surface.

As a rough guide, an uninsulated 5-gallon bath can be held near 40°C. by a 100-watt heater, and near 80°C. by 500 watts. Knife-blade heaters are convenient but, in permanent arrangements, heating elements in flexible metal tubing, shaped to fit the bath, are desirable.

3. Thermoregulators and relays of all degrees of complexity are available. Bi-metallic strips are not sufficiently sensitive, and the regulator is usually a vessel in which the expansion of a liquid (mercury) closes a contact and turns off the heater through a relay. The precision obtainable is dependent on the volume of mercury used and on the diameter of the capillary through which it rises to close the contact. In order to increase the sensitivity, an organic liquid, such as toluene (seven times the cubical coefficient of expansion of mercury) is sometimes used to

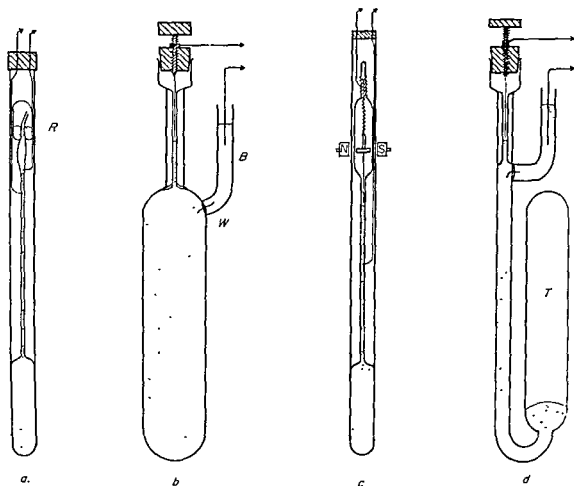


FIG. 20-3. Types of Thermoregulators. In each, mercury rises in the capillary to close the circuit. The upper contact is adjustable in *b*, *c*, and *d*. In *a*, mercury in reservoir *R* is added or removed to set the temperature. Type *b* has the fixed contact sealed through glass at *W*, and side arm *B* is filled with mercury for convenience. Types *a* and *c* are sealed systems containing an inert gas. *c* is adjusted by means of an external magnet *NS*. In *d*, space *T* is filled with toluene to increase the sensitivity.

move the capillary mercury. The mercury column may also be driven by the changing vapor pressure of a volatile liquid. Mercury regulators can give exceedingly precise switching action, but are subject to oxidation and sticking at the contacts. This is especially true when organic liquids are used in conjunction, or if arcing occurs as the contact is broken (use of too high a voltage). Unless sealed under inert gas, the contacts may require periodic cleaning. Many narrow-capillary regulators are prone to the mercury "hanging up" above the contacts or on the glass walls, and a small, continuous vibration is helpful in obtaining positive action.

It is highly desirable to be able to adjust the position of the upper contact by a screw action (Fig. 20-3*b, c, d*). This permits rapid adjustment of the apparatus to the desired temperature null point. Regulators in which only the volume of mercury can be changed (as in a Beckmann thermometer) are very tedious to adjust to a predetermined temperature.

In order to prevent corrosion at the point of contact, only very small currents should be passed through a mercury thermoregulator. The heater current is usually switched on and off by a vacuum tube or transistor activated relay circuit. Many circuits include a condenser to add a time-lag to the on-off switching, and thus prevent chattering of the relay contacts. In more elaborate circuits, thyatron tubes can be used to supply power to the heaters in proportion to the demand of the system.

Thermoregulators in which a thermistor replaces the mercury expansion switch are also available. The thermistor (placed in bath) is made one arm of a Wheatstone bridge, and its change in resistance with temperature is used to drive a thyatron relay circuit. The temperature of regulation is selected by adjusting variable resistors in another arm of the bridge. Such a unit can be used under widely varying bath conditions and eliminates mechanical regulation problems.

A very convenient alternative to the conventional regulator-relay-heater arrangement is the use of a relay which operates on changes in capacitance. An external capacitance lead wire is simply clipped to the (ordinary) bath thermometer near the temperature desired. When the bath reaches the proper temperature, the relay circuit capacitance is balanced to provide on-off regulation at this point. The changing level of mercury (liquid) in the thermometer stem changes the capacitance of the circuit and induces the relay on-off action. With reasonable care in shielding the leads, the precision obtained is governed simply by the precision of the thermometer used.

*Air and Vapor Thermostats.*—These thermostats are generally less satisfactory than liquid baths and are most useful at high temperatures. Air baths can be classified either as the "furnace" or the "convection" type.

Convection baths are analogous to liquid thermostats in that a heater, a circulating fan, and a thermoregulator are used. Any operational problems stem from the low heat capacity of the air and the need for insulation and good internal circulation. Temperature control is usually in the range  $\pm 0.1$ – $0.5^\circ$  up to  $400^\circ\text{C}.$ , and bimetallic regulators are used.

"Furnace" type thermostats are usually smaller, electrically wound chambers in which no regulator or circulating fan is used. Radiation from the walls provides temperature uniformity within the cavity and a simple balance of electrical input with normal heat losses maintains the constant temperature.

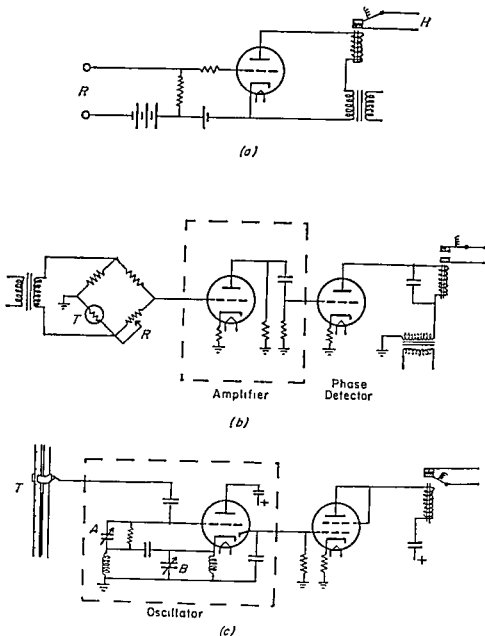


FIG 20-4. Simplified Relay Control Circuits.

a. For use with a mercury regulator. Current is normally flowing through the tube-relay circuit. When the regulator closes the circuit at  $R$ , the grid becomes negative and the relay current is stopped, shutting off the heater supply  $H$ .

b. Thermistor  $T$ , which changes resistance markedly with changing temperature, is placed in the thermostat and is made one arm of a Wheatstone bridge. The "balance" point (temperature) is selected at  $R$ . When the temperature changes, the bridge becomes unbalanced and the output signal is out of phase. After amplification, the direction of phase change (corresponding to higher or lower temperature) is detected by a tube which has A. C. on its plate; the tube conducts only when the grid has the proper sign.

c. This capacitance sensitive circuit consists of a weak oscillator whose null point is selected at  $a$  and  $b$ , and which biases the grid of a relay tube, thus preventing it from conducting. Mercury rising in the thermometer  $T$  increases the capacitance in the "antenna," stopping the oscillation. The bias on the relay tube is then removed, and it conducts through the relay which shuts off the heater.

Thermostats in which the sample is bathed in the vapor of a boiling liquid can provide excellent temperature control, but are usually limited in size. In a simple

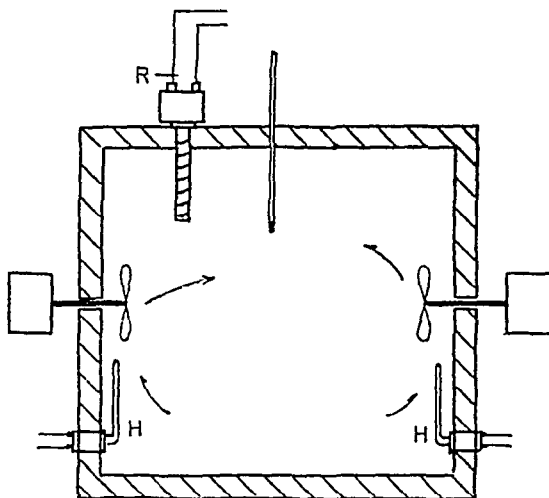


FIG. 20-5. Air-Bath Thermostat. Heaters *H* are controlled by bimetallic Regulator *R*.

arrangement, the sample is held in a "finger" which extends into the refluxing liquid.

Some insulation is required to minimize the effect of air drafts. If the total volume of liquid is fairly large, mixed liquids can be used as well as pure ones,

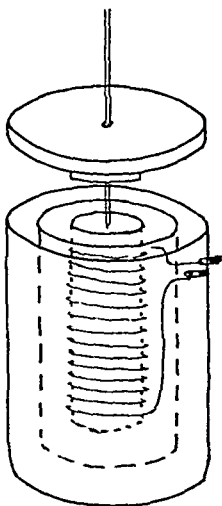


FIG. 20-6. Furnace-Type Thermostat. The inner cylinder or block is wound with resistance wire and is surrounded by layers of insulation and metal radiation shields.

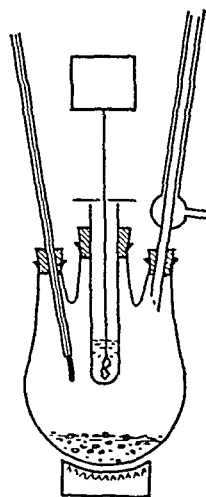


FIG. 20-7. Vapor-Bath Thermostat  
Made from a Three-Necked Flask.

and the temperature can be selected by adjusting the composition. The apparatus works well above about 70°C., and alcohols, toluene, water, acetic acid, etc., or their mixtures can be used. Temperature control is about  $\pm 0.1$  to  $0.2^\circ$ .



Much more precise control can be achieved if the apparatus is carefully jacketed and the outlet of the reflux condenser is connected to a manostat. A range of temperatures is then obtainable from a single (pure) refluxing liquid by a simple adjustment of the pressure.

**Low-Temperature Thermostats.**—The most versatile arrangement for low-temperature thermostating is the use of a mechanical refrigerator with a conventional liquid bath. Some effort must be made to insulate and cover the bath in order to prevent excessive condensation. Portable refrigerators are available with an expansion coil that can be placed directly into the thermostat. The thermoregulator is then used to turn the refrigerator on and off as needed.

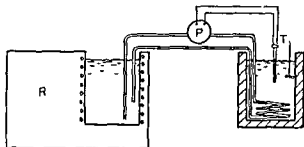


FIG 20-8. Cooling a Thermostat by Circulating Liquid Through a Coil. Thermoregulator  $T$  controls pump  $P$ , drawing liquid from refrigerator  $R$ , as needed.

Another arrangement that yields somewhat better control consists of refrigerating a large volume of liquid at a very low, but not necessarily known, temperature. This liquid is then used to cool the thermostat, by circulating it through a copper coil in the thermostat bath. The thermoregulator controls only a small circulating pump, and the on-off load on the refrigerator is considerably lessened.

For short-term experimentation, excellent low-temperature control can be obtained in baths of melting ice ( $0^\circ$ ) or mixtures of dry ice and acetone ( $-80^\circ$ ).

$0^\circ$ —Melting ice Use a Dewar flask. It is important that the bath be full of crushed (and pure) ice plus water, not just ice alone. Regular additions of ice are needed, and a stirrer reaching to the bottom of the flask should be used to keep water beneath the floating ice at  $0^\circ$ . Control of  $\pm 0.01^\circ$  is relatively simple.

$-80^\circ$ —Dry ice and acetone A Dewar flask is essential. Temperature control is very good and only dry ice must be added from time to time. No stirrer is needed.

In theory, a large number of different low temperatures should be attainable through the use of various ice-salt-water eutectics. In practice, most of these eutectics do not provide satisfactory temperature control. In some cases the saturated solutions are very viscous and do not come to equilibrium sufficiently rapidly. In others, metastable solid phases are formed, or hydrates do not undergo transitions rapidly, and the temperature is not constant. Except possibly for simple systems, such as those below, the use of salt eutectics is not recommended.

- $-21.1^\circ$ —Ice + NaCl + water. Use a Dewar flask and start with only ice and salt. Stirring is essential to keep the solution saturated with salt as the ice melts. Both ice and salt must be added periodically. Scratch the container to ensure formation of the stable dihydrate  $\text{NaCl} \cdot 2\text{H}_2\text{O}$ .
- $-17.7^\circ$ —Ice +  $\text{NaNO}_3$  + water (no hydrates)
- $-15.4^\circ$ —Ice +  $\text{NH}_4\text{Cl}$  + water (no hydrates)

A fairly large number of common organic compounds freeze between  $0^{\circ}$  and  $-50^{\circ}\text{C}$ . and are potentially useful as constant-temperature baths. The usual method is to stir in fine chips of dry ice until about half the mass has frozen and a constant temperature is attained. However, many of these compounds have low heats of fusion, and the baths require considerable attention during use. A half-frozen mass of ethylene glycol for example, will hold about  $-17^{\circ}$ , but condensation of water vapor from the air tends to make this temperature vary. Some compounds (e.g.,  $\text{CCl}_4$ ) have allotropic forms near the melting point and yield only approximate control. On the whole, melting organic solvents are not suitable as high-capacity cryostats.

### SAMPLING

Samples of a saturated solution taken for analysis should be filtered as a routine procedure. This is especially important when the solid settles very slowly, or

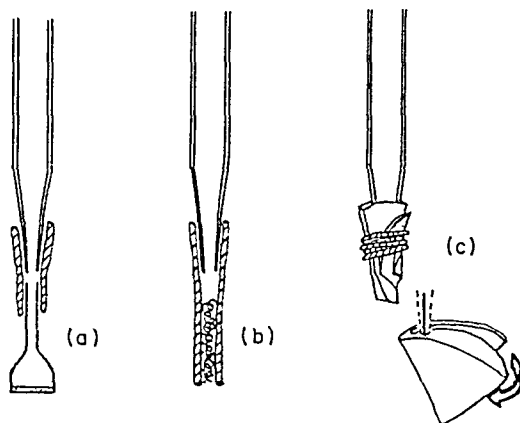


FIG. 20-9. Filter Tips Attached to Pipets. *a*. Sintered glass filter attached with rubber tubing. *b*. Rubber tubing with glass wool or cotton. *c*. Filter paper folded about tip and held with rubber band.

when it is finely divided or transparent. Aside from accidental introduction of solid, precautions must also be taken to prevent cooling (precipitation of solid) or evaporation of the solvent.

Sampling with a pipet and suction is often quite satisfactory and can be used as a simultaneous determination of the density. Simple, removable filter "tips" may be made from sintered glass, glass wool, or filter paper held by rubber bands. If the solubility is being determined above room temperature, the sampling pipet should be heated to prevent crystallization before the transfer is completed. Simply preheating the pipet in an oven may be satisfactory, but insulating the bulb or wrapping with electrical heating tape is more efficient.

The sample is usually delivered into weighed flasks, some care again being taken to prevent evaporation of the solvent. If very small samples must be taken, or if cooling and crystallization cannot be avoided, it is convenient to use preweighed



FIG. 20-10. Specific Gravity or "Weight" Pipet.

"weight pipets" from which the sample cannot spill; the whole pipet can be weighed at leisure. The sample is later washed out with the aid of heat and excess solvent. These pipets are often small enough to be completely immersed in the solution during sampling, thus eliminating temperature variations.

Under certain conditions, it is preferable to use pressure rather than suction to take samples, and special apparatus can be devised to work entirely within the thermostated bath. If an inert atmosphere is being used, if the solvent is volatile, or if sampling will take a long time (if filtration is slow, for example), the arrangement shown in Fig. 20-11a may be desirable.

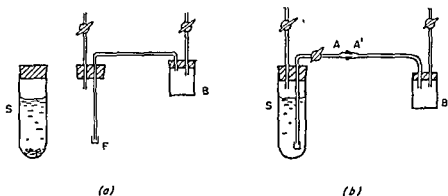


Fig. 20-11. Apparatus for Sampling at Constant Temperature or Under Inert Atmosphere. S, solubility tube; F, filter tip; B, sample bottle.

After the solubility tube has been tumbled to attain equilibrium, the mouth is brought above the level of the bath and the stopper removed. The "fitted" stopper is then quickly substituted and the sampling done by forcing solution over into the sample bottle. The whole assembly can be lowered back into the bath to maintain constant temperature during the transfer.

If the stopper substitution step will lead to errors, the same type apparatus can be divided as in Fig. 20-11b. The solubility tube is already fitted with pressure inlet and filter tube. The connection AA' is made above the bath level and then resubmerged. Obviously, many other variations and adaptations of these techniques are possible.

## ANALYTICAL METHODS

All of the common physical and chemical analytical techniques have been used to determine solubilities. The simplest method is to evaporate the solvent and determine the weight of the residue. This can be done very accurately if the solution is concentrated and the solute is stable during drying. The density of the saturated solution should be determined as a matter of routine.

With very insoluble materials, a physical method of analysis is often the best choice. A large amount of work has been based on e.m.f. and conductivity measurements. Radiotracers and polarography are also valuable, but a number of solubilities reported by these methods have proven unreliable. With slightly soluble materials, great care must be taken to exclude impurities from both the solvent and the solute, or the measured "solubility" may be grossly in error. Greater care must also be taken during sampling in order to eliminate traces of suspended solute.

When a moderately soluble solute is being studied, it is sometimes possible to observe the approach to equilibrium without sampling and analyzing the liquid. A graduated float, for example, can be used to (continuously) measure the density as the dissolution proceeds. Electrical methods have been used similarly.

### FACTORS INFLUENCING THE RATE OF ATTAINMENT OF EQUILIBRIUM

The time required to reach equilibrium can vary widely from system to system, but certain generalizations can be made. The rate of dissolution of a solute in a given solvent depends primarily on the temperature, the surface area of the solute,

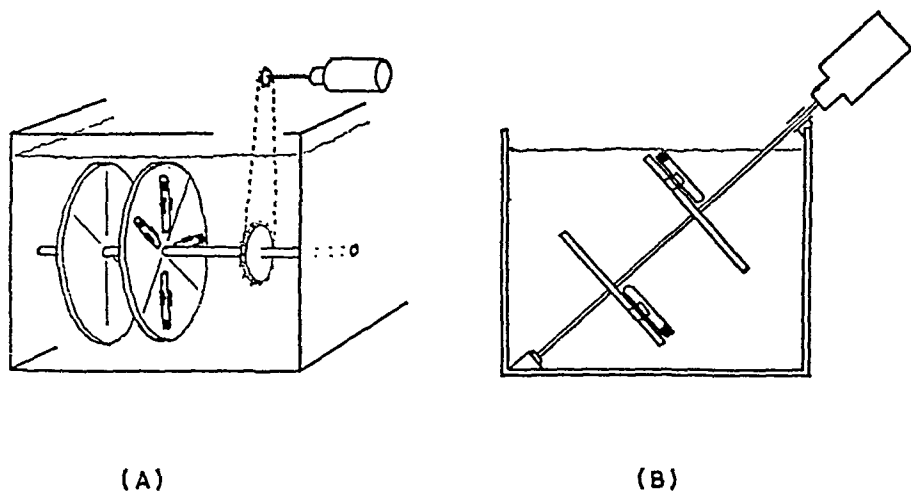


FIG. 20-12. Solubility Tubes Attached to Rotating Wheels.

and the degree of agitation. There is no simple relationship between the solubility of a substance and the rate at which equilibrium is approached. Soluble salts are often said to dissolve more rapidly than insoluble ones, but this is a rather subjective observation, and there are many exceptions. For example, the insoluble silver halides equilibrate with water at least as rapidly as does silver nitrate.

The rate of dissolution is usually determined by the rate of removal of saturated liquid from the surface of the dissolving solute. Thus, the factors which increase the rate of removal—good agitation, high temperature, and low viscosity—are the ones most important in producing rapid equilibration.

**Agitation.**—Some sort of agitation must be provided in all solubility determinations. If a number of experiments must be done at the same time, an “external” shaker or tumbler is most economical. The sealed tubes or flasks can be clamped in position and one motor used to turn them all. Submerged, rotating wheels (with clamps) are used to give long-term continuous operation. When the saturation tubes are to be tumbled in this way, it is good practice to place a glass marble inside, in order to break up and mix the components. Sometimes steel balls or mercury are used if the solution is very dense or viscous.

All sorts of shakers and rockers have also been devised. One satisfactory arrangement based on a commercial shaker is shown in Fig. 20-13a. In this arrange-

ment, it is important to keep the samples as far below the thermostat bath level as possible.

When only a few determinations are needed, internal stirring with a propeller may be most satisfactory. With direct-drive stirrers, some sort of seal is needed to prevent losses by evaporation. Sometimes a flat bottom flask can be used and a magnetic stirring bar put inside. This eliminates troublesome rotating seals, but the magnetic field unit is then somewhat difficult to place. One satisfactory arrangement (provided the bath is not made of steel) is shown in Fig. 20-13b.

**Temperature.**—Although a given solute-solvent pair can be expected to equilibrate more rapidly at higher temperatures, heating cannot always be recommended. There is considerable danger that the heating may be carried too far and that a supersaturated solution may be formed. Even when excess solid is present, some

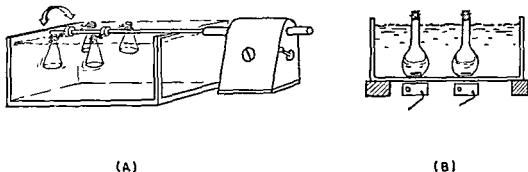


FIG 20-13 a Agitating Flasks with a Shaker. b. Internal Stirring with Magnetic Bars. Rotating Fields Are Placed Beneath the Bath.

supersaturated solutions come to equilibrium very slowly. Further, heating may cause an undesired (and unnoticed) solid phase change (e.g., dehydration), which may or may not be reversible.

On the other hand, heating to form purposely a supersaturated solution is an invaluable way of approaching equilibrium from "two directions." If the solubilities from "under" and supersaturations agree, equilibrium is assured.

**Particle Size.**—For practical purposes, the solubility may be considered independent of the particle size of the solute. Very fine particles, and freshly precipitated materials, have been found to have higher solubilities than coarser samples, but most finely divided solids age and grow rapidly and reach a stable equilibrium. Only with obviously "colloidal" solids need this effect be considered.

Fine crystals, of course, will reach equilibrium more rapidly than large ones, which is desirable. On the other hand, very fine crystals may settle slowly and be hard to filter during sampling. A few accidental solid particles can produce large errors in the analysis of dilute solutions.

**Viscosity Effects—Polymers.**—The great majority of systems will reach equilibrium in from a few hours to a day of stirring. In very viscous solutions, however, mixing and diffusion can be so slow that weeks or months are required to attain equilibrium. Solutions in glycerin, glycols, or those containing organic high polymers fall in this category. Inorganic species such as silicates, phosphates, borates, and iodates also form viscous solutions because of their polymeric nature. Concentrated solutions of "simple" salts may become very viscous at temperatures below 0°. Supercooling of such solutions is the rule, and equilibrium should be approached from undersaturation whenever possible.

**Other Rate-Determining Factors.**—In certain systems the approach to equilibrium is slow and the “amount dissolved after a given length of time” may have more practical significance than the true “solubility.” Examples might be substances which decompose or hydrolyze slowly, or which react with oxygen or carbon dioxide. It should be remembered that solids that have been sintered (e.g.,  $\text{CaSO}_4$ ) may require a very long time to become rehydrated. In general, changes involving solid phases (solvation, solid solution formation) are much slower than those in the liquid. Compounds that are surface active, whose surface concentration differs from that in bulk, and compounds that associate in solution also equilibrate relatively slowly.

## ESTABLISHMENT OF EQUILIBRIUM

**Constancy of Composition.**—The simplest and the most widely used criterion of equilibrium is constancy of solution composition. The solute (solid) is stirred or shaken with the solvent continuously, and samples are removed after varying periods of time. When successive analyses show no further change in composition, equilibrium between the phases has been attained. Constant composition with time does not, however, guarantee that (1) the starting material was pure, (2) slow changes are not occurring, or (3) the equilibrium is “stable” with respect to some other possible phase in the system.

**Approach from “Two Directions.”**—A considerably more rigorous test of equilibrium is to approach the same set of conditions from two different directions. If the solubility found from supersaturation is the same as that from undersaturation, equilibrium has been proven. The supersaturated solution is obtained by heating until excess solid has dissolved. The solution is then allowed to cool (with crystals present) in the thermostat. As a rule, the approach from supersaturation is slower than from undersaturation, even when enough crystallization nuclei are at hand. The difference between the equilibrium concentrations from under- and supersaturation is a fair measure of the reliability of the experiments, and the average value is usually taken as the solubility.

When the system has three components (two solids plus solvent, or one solid with a mixed solvent), results can be obtained from two composition “directions.” For example, the solvent can be saturated with solid *A* first, and then *B* added, or vice versa. This technique is especially useful when the solid phase is itself undergoing a change, such as solid solution formation.

**Purity of the Saturating Solid.**—If it is necessary to prove that the solute is “pure” and to know the true solubility, other techniques must be employed. One useful procedure is to determine the equilibrium “solubility” in two mixtures which contain widely different ratios of solute to solvent. If a soluble impurity is present, its concentration in the resulting two saturated solutions will be different and will alter the solubility of the solute in each to a different extent. (The impurity may either increase or decrease the solubility of the main solute: insoluble compounds often become more soluble in the presence of foreign materials, very soluble compounds usually become less soluble.)

One way of obtaining the solubility of the pure solute is to “leach” it with successive portions of fresh solvent and determine the equilibrium concentration each time. The impurity should eventually all be removed, and the solubility will thereafter remain constant, which will indicate that the saturating phase is pure.

## IDENTIFICATION OF THE SATURATING PHASE

**Composition of Solid Phase.**—The determination of "the solubility" implies a knowledge of the composition of the solid phase. If the solid(s) is changing, it may be necessary to re-analyze it either directly or indirectly in order to be able to interpret the results. If the solubility of an inorganic salt is being determined in a water-alcohol mixture, for example, the formation of a solid alcoholate may change the composition of the solvent markedly. Similarly, the addition of a third component may change the degree of hydration of a salt and may alter the interpretation of the data. The formation of solid solutions, double salts, and hydrolytic "basic" salts are all relatively common complications.

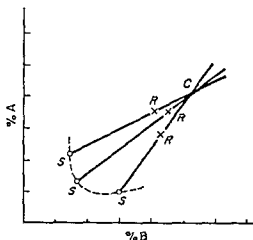


FIG. 20-14. Determination of Solid Phase Composition by the Intersection of Tie-Lines.  $S,S,S$  compositions of saturated solutions;  $R,R,R$  compositions of the corresponding wet residues. Lines  $S-R$  are tie lines;  $C$  is the composition of the saturating solid.

There are several methods of identifying solid phase changes that are routinely employed in studies of phase equilibria. Direct chemical, physical, or microscopic analyses of the solid are obvious; the only problems involve removal of the saturated liquid and the prevention of changes during handling (evaporation, temperature, oxidation). When the work is being done at high or low temperatures, or in viscous solutions, these problems may become very great, and an indirect analysis is often the only recourse.

The fundamental technique in indirect solid phase analysis is Schreinemaker's "Wet Residue" analysis. In this method, no attempt is made to dry or remove the solution from the sample of the solid

phase. The wet solid is analyzed for each component, as is the saturated solution. The composition of the dry solid is then calculated by "subtracting" the composition of the solution from that of the mixture. In order to do this the amount of liquid wetting the solid must also be known. One way of knowing this is to use a small amount of an inert "trace" compound that stays entirely in the liquid phase. The amount of the tracer found in the wet mixture indicates the amount of solution retained.

Convenient graphical and algebraic methods can be used when the system contains more than two components. In these, the solution and wet residue compositions are plotted, and a straight line drawn through them (a "tie-line") also passes through the composition of the solid phase. The intersection of several such tie-lines indicates the unknown composition.

A convenient variation of the wet residue method involves the preparation of mixtures of solvent and solutes of precisely known composition. After equilibrium is established, only the saturated liquid is analyzed. The original (total) composition of the mixture can then be used as a point to fix the tie-line instead of analyzing the equilibrium wet residue.

**"Stable" vs. "Metastable" Equilibrium.**—Although these analytical techniques can establish the existence and reversibility of an equilibrium solubility, they can-

not necessarily distinguish between stable and "metastable" equilibria. Unless the change is observed experimentally, there is no way of determining whether a system is metastable (or "unstable") with respect to some other solid phase. Saturated solutions of sodium sulfate, for example, can be in true reversible equilibrium with the anhydrous solid at room temperature, even though the decahydrate is the "stable" phase below 32°C. The solid phase transition may not occur for weeks unless decahydrate seeds are introduced, and only then is it evident that the solubility curve of the anhydrous salt is metastable.

Methods which can be used to induce formation of the stable phase are (1) addition of "seed" crystals of the stable phase or of a similar compound which may have similar crystal structure, (2) vigorous scratching of the (glass) walls of the container, (3) heating or cooling (plus scratching) in the hope that a stable phase may form more readily at higher or lower temperatures.

### "SYNTHETIC" OR "POLYTHERMAL" METHODS

In a "synthetic" or "polythermal" determination of solubility, a mixture of known amounts of solute and solvent is prepared and is heated slowly until all of the solute has dissolved. At the temperature where the last trace of solute disappears, the saturated solution has the composition of the prepared mixture, and the "solubility" is thus known. In other variations of the method, a solution may be cooled until the first crystals or cloudiness appears, or the heat capacity of a mixture may be followed by a cooling curve, as in freezing-point determinations.

The "synthetic" method has the advantage that no analysis of the saturated solution is necessary; the composition can be known to any desired accuracy in the preparation of the mixture. Tedious or inaccurate analytical procedures can thus be avoided.

Since strictly isothermal conditions are not required, the synthetic method does not require elaborate thermostating equipment. It is well suited to systems that contain a volatile or air-sensitive component in which sampling would be difficult. The synthetic method is often used when only small quantities of material are available; the substances are weighed into a capillary, sealed, and observed microscopically. Finally, the synthetic method is extensively employed in very high- or very low-temperature work where sampling is nearly out of the question. The phase changes are deduced from changes in heat capacity on cooling or heating curves.

Although the synthetic determination of solubilities is sometimes the logical choice, it has definite limitations. It does not, for example, reduce the need for utmost care in assuring that equilibrium has been attained. The solution must be well agitated, and must be held at each temperature long enough to become saturated. If the solution is viscous or if the solid phase is changing composition, the usual isothermal saturation method is faster and more satisfactory. The method is not suited for use with surface-active materials, or with very insoluble compounds.

*Procedure with Readily Soluble Solids.*—The solvent and the finely divided solid are weighed into a tube or flask and placed in a (water) bath whose temperature can either be raised continuously or can be held constant as needed. A stirrer and precision thermometer are fitted to the flask. The solution is stirred at the bath temperature until no further solid appears to dissolve (at least one-half hour). The temperature of the bath is then raised a fraction of a degree per minute. When only a few crystals of solute remain, the rate of heating is slowed down (to



less than  $0.1^{\circ}$  per minute), and for best results the temperature should occasionally be held constant to ensure saturation. The heating is continued until the last traces of crystals are about to dissolve. The accuracy of the method depends on the length of time allowed for equilibration as the final temperature is approached. A second determination on the same mixture is made by chilling to precipitate the solid, and then reheating. With care, reproducibility to about  $\pm 0.2^{\circ}\text{C.}$  can be obtained. Unless the solid has an unusually high-temperature coefficient of solubility, the allover accuracy can be fairly good. The method suffers in being time consuming and in requiring continuous observation.

It should be noted that the precise solution temperature cannot be obtained by cooling a solution to the first appearance of crystals, because supersaturated solutions will almost invariably be formed. Replicate determinations must always be made from the direction of undersaturation.

**Use of Cooling and Heating Curves.**—Although cooling and heating curves can be used with high precision if the appropriate apparatus is available, they are generally less useful than other methods in routine solubility determinations. Accurate work requires that a constant temperature differential be maintained between the solution and the bath, and the rate of cooling or heating of the solution is plotted. These rates are often too fast for the solid-solution equilibrium to follow satisfactorily. Excellent precision can be obtained when ice is the phase crystallizing from a solution, for example, but the heat capacity of many other compounds is relatively low, and thermocouples rather than glass thermometers must be employed.

## SOLUBILITY OF LIQUIDS IN LIQUIDS AT CONSTANT TEMPERATURE

**The Analytical Method.**—The major differences between solid-liquid and liquid-liquid solubility determinations are that:

1. With two liquids, the solubilities are reciprocal. That is, some of each liquid always dissolves in the other, and both liquids must be analyzed in order to describe the system properly.

2. Liquids attain solubility equilibrium much faster than do solids, and 5 or 10 minutes of shaking is usually all that is required. Conversely, good temperature control must be maintained at all times.

3. Certain difficulties are experienced because of the volatility of the liquids. In order to prevent pressure build-up during agitation, only a small "free" air space should be left. If possible, the free space should be allowed to fill with solvent vapor before sealing the solubility vessel.

Unless the liquids form stable emulsions, they should be agitated vigorously to provide thorough mixing and high surface area of contact. If emulsions tend to form, or foams are produced at the interface, then only gentle mixing can be used and correspondingly more time is needed for equilibration.

When the liquid layers have separated, samples of each layer are taken for analysis with pipets inserted to the proper level. Samples of the bottom layer can be taken without contamination from the top layer by using a clamp or stopcock, or by maintaining a very slight positive pressure of air while lowering the pipet tip through the upper layer.

**The Synthetic Method.**—This method is based on measuring the volume changes of the two liquid phases as they equilibrate with each other, and can be applied to any liquids that separate to form a sharp interface after mixing. Graduated cylinders, burets, or specially constructed flasks are used.

Two separate mixtures of the two liquids  $L_1$  and  $L_2$  are prepared, and the original weight of each liquid is measured. In the first mixture a large amount of liquid  $L_1$  is used with a small amount of  $L_2$ , and in the second mixture it is the reverse—a large amount of  $L_2$  with a small amount of  $L_1$ . Each mixture is then thoroughly mixed and allowed to separate. The volumes of the top and bottom layers are then read.

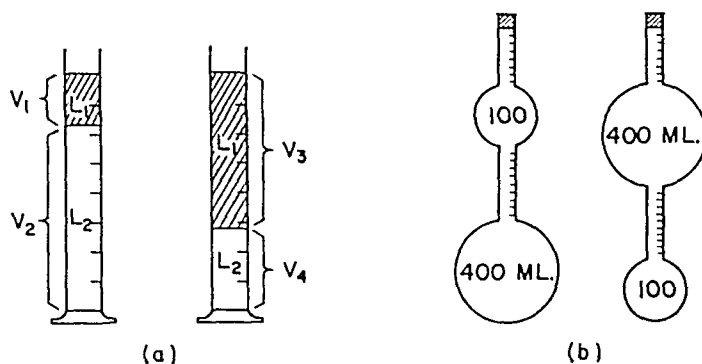


FIG. 20-15. a. Graduated Cylinders Used to Measure Liquid-Liquid Solubilities. b. Flasks Designed for Greater Accuracy.

Even though the relative proportions of the upper and lower layers differ, the compositions of the upper and lower layers in the two mixtures are the same (the solubility of each liquid in the other is a constant at a given temperature). The total (original) amount of each liquid is now distributed between the two layers, and if

$x$  = concentration g./ml. of  $L_1$  in the upper layer

$y$  = concentration g./ml. of  $L_1$  in the lower layer

then

$$\text{Total wt. } L_1 \text{ in the first mixture} = xV_1 + yV_2$$

Similarly:

$$\text{Total wt. } L_1 \text{ in the second mixture} = xV_3 + yV_4$$

These equations are then solved simultaneously for  $x$  and  $y$ . If the densities of the equilibrium upper and lower layers are also determined, the concentrations (grams per milliliter) can be converted to a strictly weight basis.

This method can be used with high accuracy if specially constructed bottles are employed. These bottles hold relatively large (calibrated) volumes, but the meniscus levels are read in narrow tubes. More time and care must be taken in the equilibration of the phases, however, because of the constricted design of the flasks.

**The Cloud-Point Method (Synthetic).**—The synthetic “cloud-point” method is often used in the determination of liquid-liquid solubilities as a function of temperature. Equilibrium is rapidly attained and the “end point” is easy to observe.

The usual approach is to weigh appropriate amounts of the two liquids together and to then heat (or cool) until a single homogeneous phase is formed. The temperature is then slowly lowered (or raised) until the second liquid layer is seen to separate out. This is an approach from the direction of oversaturation, but liquid phases do not tend to supersaturate. The formation of the droplets of the second liquid occurs throughout the entire solution and gives the whole a "cloudy" appearance. This "cloud-point" change usually can be observed with both rising and falling temperature, and can be determined to about  $\pm 0.2^\circ$ .

The single cloud-point determination does not yield the composition of the second (cloud) liquid phase. If the temperature of phase separation is determined over the entire range of composition (0–100%) of the two liquids, and a smooth curve drawn through the points, then the compositions of the phases coexisting at any given temperature can be read from the graph.

### SOLUBILITY OF GASES IN LIQUIDS

Gas solubility measurements are subject to many errors of manipulation. In addition to thermostating, the total pressure must be controlled, the vapor pressure of the solvent must be known, and the solvent (and apparatus) must be free of foreign gases. Special care must be taken to eliminate gas leaks and to keep the vapor space saturated with solvent.

The solubilities are usually expressed as:

$l$  = the Ostwald coefficient which is the volume of gas (measured at the temperature and pressure of the experiment) absorbed by one volume of solvent.

$\beta$  = the Bunsen coefficient which is the volume of gas (corrected to  $0^\circ$ , 760 mm) absorbed by one volume of solvent.

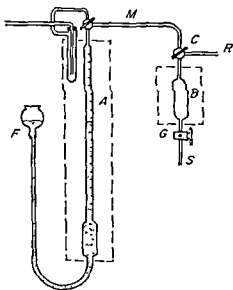


FIG. 20-16. Ostwald-Type Gas Absorption Apparatus.

As these coefficients imply, most gas solubilities are measured by volumetric means. With very soluble or reactive gases, however, direct weighing, titration, etc., are entirely feasible. Often the solute gas can be swept or distilled out of the saturated solution and analyzed independently.

In the standard absorption method originated by Ostwald, a gas buret ( $A$  in Fig. 20-16) is connected by capillary tubing  $M$  to an absorption flask or pipet  $B$ . The dimensions of  $A$  and  $B$  must be chosen with due regard to the solubility of the gas being measured. Great care must be taken to prevent gas leaks and both the buret and pipet are thermostated for best work. If only the pipet is thermostated, temperature corrections for the portion of the gas in the buret must be made. The solvent is thoroughly degassed by boiling, and is drawn up under vacuum through  $S$ . When  $B$  is full, the apparatus is flushed with the solute gas, which is removed through three-way stopcock  $C$  and tube  $R$ . Buret  $A$  is filled by lowering mercury reservoir  $F$ . A por-

tion of the gas is passed into the absorption pipet by raising *F* and opening *G*. The volume of solvent forced out through *G* is measured. The volume of gas in the pipet equals that of the liquid displaced; the volume of liquid remaining is calculated from the known volume of the pipet. Stopcock *C* is closed, and the pipet (or whole apparatus) is shaken to mix the gas with the liquid; *C* is then opened to allow gas from the buret to enter and replace that absorbed. This

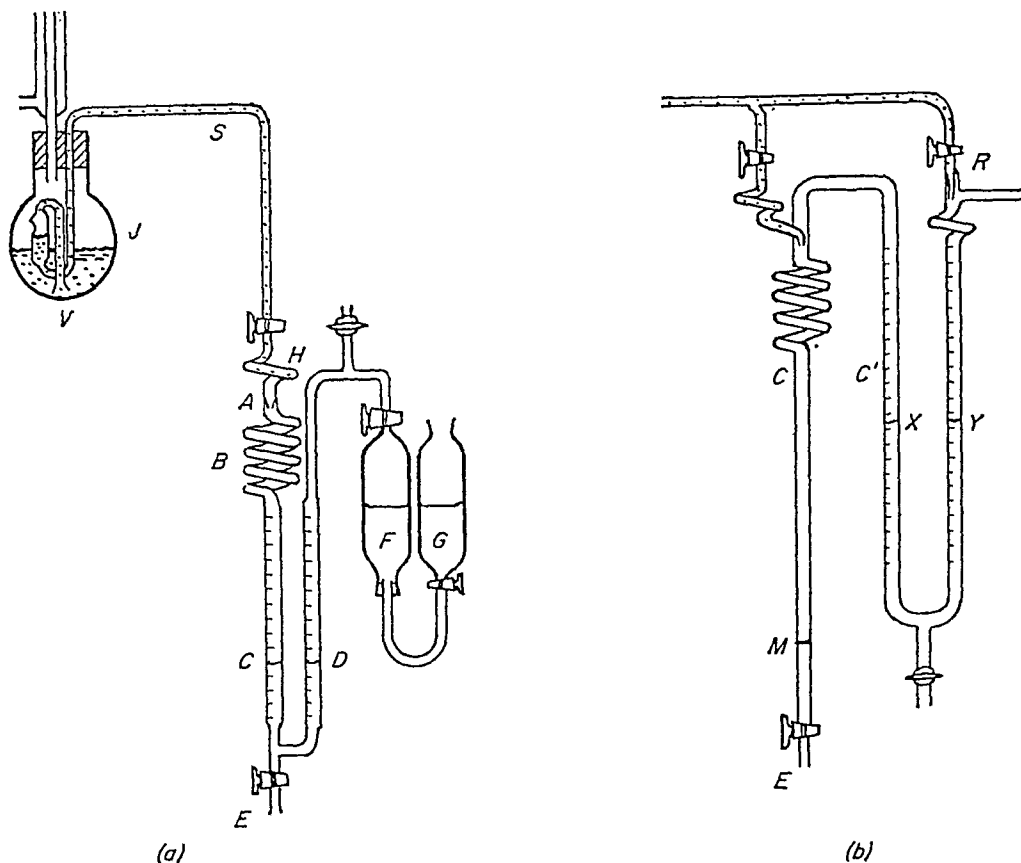


FIG. 20-17. *a.* Film Absorption Apparatus of Morrison and Billett. *b.* Modification Permitting Study of Very Soluble Gases.

process is repeated at 5- to 10-minute intervals until, upon opening *C*, there is no further decrease in volume in *A*. The absorption coefficient is then calculated, taking into account the partial pressure of the solvent. With careful work, precision of better than 1% is obtainable.

An important variation of the volumetric method was introduced by Morrison and Billett (Fig. 20-17*a*). In this apparatus the solvent is added continuously, and the film of liquid rapidly comes to equilibrium with the gas. No agitation is required, and the precision of the measurements is excellent.

The solvent is boiled out in *J*, which contains a vapor-pump *V*, and is siphoned into the apparatus through the constant-level siphon *S*. The liquid drops into the gas-filled chamber at *A* and flows through spiral *B* where it becomes saturated. Saturated liquid is collected from *E* just fast enough to keep the levels in *C* and *D* the same. Readings of the level *C* and the volume of liquid from *E* are made:

$C$  measures the volume of gas absorbed;  $E$ , plus the accumulation at  $C$  and  $D$ , is the volume of solvent.

Tube  $D$  is filled with gas, and  $F-G$  assures that the pressure is constant throughout. The spiral  $H$  is used to preheat the solvent for work at high temperatures, the absorption section is thermostated.

Using a spiral  $B$  made from 10-mm. tubing, and  $C$  and  $D$  from 50-ml. burets, a drop rate of about 2 cc. per minute through  $A$  was generally found to be satisfactory. The method has the advantage that fresh solvent is constantly being used, that equilibration is rapid, and that a large number of readings can be made. When the volume of gas dissolved is plotted against the volume of solvent used, a straight line must result.

When solubilities of very soluble gases are to be measured, the adaptation shown in Fig. 20-17*b* has been employed. The gas buret  $C$  has been enlarged to include the volume  $C'$ . Solvent is also added at  $R$  to keep the levels  $X-Y$  equal and thus maintain constant pressure. Readings at  $E$  (collected liquid) and at  $X$  and  $Y$  are made when the liquid level in  $C$  is at a fixed mark  $M$  (controlled by the flow through  $E$ ). An all-over precision of 0.5% is attainable.

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## Chapter 21

# DETERMINATION OF WATER

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Literally hundreds of methods have been proposed for the determination of water in solids, liquids, or gases. Procedures have been developed based on the high chemical reactivity of water, its electrical and physical properties, and its absorption characteristics.<sup>1,2</sup> In the current brief review, the more widely used techniques for the analysis of commercial materials are discussed. General procedural information is given for several methods. However, for operation of commercially available instruments, the reader is referred to the manufacturers' literature.

**Karl Fischer Reagent (KFR) Method.**—The liquid or solid sample, containing up to 250 mg. of water, usually is dispersed or dissolved in an inert liquid, such as methanol or pyridine, and titrated in a desiccant-protected system with KFR<sup>3</sup> equivalent to about 3.5 mg. water per ml. of KFR. (The solvent may be pre-titrated to eliminate a blank correction.) During titration the color of the solution remains canary yellow as long as unreacted water remains. After all of the water is consumed, the color changes to brown due to the presence of unreacted iodine. Thus, the reagent serves as its own indicator and permits visual determination of the end point with a limit of detection of about 0.5 mg. of water. Considerably lower limits of detection are obtained by electrometric determination of the end point, using the "dead-stop," potentiometric, amperometric, or coulometric technique.<sup>1,2</sup> Commercial electrometric apparatus is available. Weight percentage of water is calculated as follows:

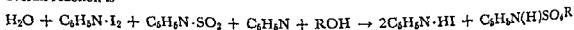
$$\text{Net ml. (sample-blank)} \times \text{mg. H}_2\text{O/ml. KFR} \times 100 \div \text{g. sample} \times 1000.$$

Water in insoluble materials often may be determined more readily by extraction at room or elevated temperature prior to titration with KFR. For example, about 97% of the moisture in wood was extracted by methanol in 6 or more hours

<sup>1</sup> Mitchell, J., Jr., and Smith, D. M., *Aquametry*, Interscience Publishers, Inc., New York, 1948.

<sup>2</sup> Mitchell, J., Jr., in *Treatise on Analytical Chemistry*, Pt. II, Vol. I (eds. I. M. Kolthoff and P. J. Elving), Interscience Publishers, Inc., New York, 1961.

<sup>3</sup> KFR is composed of iodine, sulfur dioxide, pyridine and methanol or methyl "Cellosolve." It can be prepared in the laboratory<sup>1,2</sup> or purchased from laboratory supply houses. The overall reaction is<sup>4</sup>



at room temperature or 2 to 4 hours under reflux. Water in many plastics was extracted in about one-half hour by refluxing methanol.<sup>1</sup>

The titration can be made over a rather wide temperature range. Consequently, some condensable gases can be analyzed directly at reduced temperature, e.g., butadiene at 0°C. Many noncondensable and condensable gases also can be analyzed directly by passing the sample through an absorber containing a known volume of KFR. Indirect analyses can be made by scrubbing through a dry, inert liquid, such as methanol, followed by titration of the liquid with KFR.

By proper choice of reagent concentration (water equivalence), apparatus, and method of end-point detection, the range of water titrated can vary from several micrograms to several hundred milligrams. This permits analyses for water in concentrations from parts per million to 100%.

A number of substances interfere by consuming iodine and, therefore, appear as water. A few materials oxidize hydriodic acid, one of the KFR reaction products, to iodine, giving low apparent results for water. Usually, these reactions are stoichiometric; where the concentration of interfering substance is known, suitable corrections can be applied. Many compounds can be rendered inert by suitable treatment prior to titration with KFR. The following are typical interfering materials (for more details the reader is referred to footnotes 1 and 2):

Aldehydes, Ketones  
Diacyl peroxides  
Mercaptans  
Silanols

Ammonia  
Boric acid and oxides  
Metal carbonates and bicarbonates  
Metal hydroxides and oxides

The rate of interfering reaction of the active carbonyl compounds is reduced by use of KFR having a higher pyridine concentration. Interference by ammonia is eliminated by use of excess acetic acid in the solvent.

Most other materials are inert, including most acids, alcohols, esters, saturated and unsaturated hydrocarbons, halides, hydro- and dialkyl-peroxides, salts of inorganic acids, sugars and other "stable" carbonyl compounds. Standard procedures have been established for lacquer solvents<sup>4</sup> and naval stores.<sup>5</sup>

On direct titration, total water usually is determined, i.e., free plus hydrated. Often, free water can be determined in hydrates by extraction with a water-miscible liquid, such as dioxane, which does not dissolve the sample.

**Oven-Dry Methods.**—The solid or nonvolatile liquid sample, which may weigh from a few tenths of a gram to about 100 g., depending on the nature of material and expected water content, is weighed in a tared container and placed in an oven (usually 100° to 105°C. at 1 atm.). After 1 or more hours, the sample is removed, cooled in a desiccator over a suitable drying agent, such as dry calcium sulfate, and then reweighed. The process is repeated until constant weight is attained. The decrease in weight is calculated as per cent water. Ovens with built-in balances are available commercially, permitting analyses in a single step.

Conditions for drying depend on the material to be analyzed and must be established empirically for each type of substance. Paper may require only 1 hour at 100° to 105°C.<sup>6</sup> Complete dehydration of inorganic hydrates may require considerably higher temperatures, e.g., hydrated nickel sulfate becomes anhydrous at 280°C. With many solids, particularly some natural products, the rate of diffu-

<sup>4</sup> ASTM Standards, Pt. 8, 1958, p. 943. ASTM D1364-58.

<sup>5</sup> ASTM Standards, Pt. 8, 1958, p. 425. ASTM D890-58.

<sup>6</sup> ASTM Standards, Pt. 4, 1949, p. 912. ASTM D644-44.



sion of water to the surface may be quite slow and, therefore, several hours may be required for its complete removal. For procedural details on specific materials, the reader is referred to the table of contents.

The oven-drying procedure measures weight loss. Consequently, all losses are calculated as water. These may be due to other volatile compounds originally present in the sample or formed by thermal decomposition of the sample. In some cases oxidation may occur, leading to low results.

Many thermally unstable materials can be handled satisfactorily at reduced temperature by use of (1) a vacuum oven or (2) a desiccator. In the latter case the weighed sample is placed in a desiccator at room temperature and 1 atm. or less pressure and allowed to stand until a constant weight loss is obtained. This usually requires weeks or months; hence, the desiccation procedure is seldom used for other than calibration purposes. A variety of vacuum ovens are available. Usually, time requirements are increased over conventional oven drying, and conditions must be established for each type of material studied. Procedures have been proposed for a variety of dairy products, meats, drugs and partially dehydrated foods.<sup>7</sup> For biological substances, some dehydrated foods and other relatively unstable materials, lyophilization (freeze drying) is of value for removing the bulk of the water.<sup>8</sup>

**Penfield Method.**—This procedure has been used widely for determining water in silicate rocks. In the original method<sup>9</sup> 1 g. of powdered sample was placed in a test tube having one bulb blown at the closed end and another near the midpoint of the tube. Wet cloth was placed around the center bulb which served as a condenser. The end of the tube was closed with a capillary to minimize loss of water. The sample in the tube was heated with a gas burner. The evolved water vapor condensed in the center bulb. After all condensed water was driven into the bulb, the hot flame was placed midway between the bulbs and the upper portion of the tube drawn off and rounded. The tube was allowed to cool, the wet cloth removed, the outside of the tube wiped dry, and the tube weighed. Then the tube was dried and reweighed. The decrease in weight was calculated as percentage of water in the sample.

A modification of the Penfield method employed a tared filter paper placed inside the tube to collect condensed moisture.<sup>10</sup> After all of the water was collected on the paper, it was reweighed. The increase in weight was equivalent to water in the sample.

The result represented total water in the sample. Combined water was estimated by subtracting the value for hygroscopic water (obtained by drying 1 g. of sample to constant weight at 105° to 110°C.) from the total water found.

**Absorption Method.**—The gaseous sample is passed through a tared absorption tube containing a desiccant such as dry calcium sulfate, magnesium perchlorate, or phosphorus pentoxide. Increase in weight of the absorption tube is calculated as percentage of water. The technique also is applicable to solids and nonvolatile liquids from which water can be removed during passage of a dry gas. The sample is weighed into a boat and heated in an open combustion tube. Inert gas, usually nitrogen or air, is passed over the sample after drying through a tube containing the same desiccant as that used in the tared absorption tube.

<sup>7</sup> Makower, B., Chastain, S. H., and Nielsen, E., *Ind. Eng. Chem.*, **38**, 725, 1946.

<sup>8</sup> Makower, B., and Nielsen, E., *Anal. Chem.*, **20**, 856, 1948.

<sup>9</sup> Penfield, S. L., *Am. J. Sci.*, **48** (3), 30, 1894.

<sup>10</sup> Shapiro, L., and Brannock, W. W., *Anal. Chem.*, **27**, 560, 1955.

The absorption method tends to be more nearly specific for water than those methods based on weight loss. It may be more reliable for determining small amounts of water in large samples since the absorbed water is weighed directly. Interferences include other volatile compounds absorbed by the desiccant. Water formed during thermal decomposition will lead to proportionately high results.

Through proper choice of desiccant, some interferences can be avoided. For example, calcium oxide may be suitable for samples from which ammonia is evolved.

**Distillation Method.**—The sample with an excess of a suitable water-immiscible carrier, such as toluene or xylene, is placed in a distillation flask. The flask is connected to a reflux condenser having a special graduated receiver (see Figs. 21-1 and 21-2<sup>11,12</sup>). Then the mixture is heated, usually electrically, and the condensate collected in the receiver. The condensed water remains in the receiver while the carrier is returned through an overflow to the distillation flask. The collected water is measured volumetrically. Further details on procedure are given in other chapters dealing with specific products.

Routine applications of the distillation procedure date from the developments of Dean and Stark,<sup>13</sup> who devised apparatus for continuous refluxing, collection of water in a calibrated trap, and return of the carrier to the distillation flask. Their design is still used for determining water in petroleum products and other bituminous materials<sup>11,12</sup> (Fig. 21-1). Other types of traps are recommended for various applications.<sup>11,12,14</sup> Examples shown in Fig. 21-2 are for use with a carrier having a density less than that of water. In this case, water collects in the graduated portion of the trap and most of the organic (upper) layer returns through the side arm to the distillation flask. The most commonly used carriers are benzene, toluene, and xylene, the first two forming heterogeneous azeotropes with water.

For special cases, e.g., where flammability is a problem, chlorinated materials are used, such as carbon tetrachloride and tetrachlorethane. Since these materials are heavier than water, a trap must be used which permits return of the lower organic layer to the distillation flask. The traps,<sup>14</sup> shown in Fig. 21-3, are illustrative of designs permitting return of the lower layer.

The distillation procedure has been used widely for determining moisture in grains, leather, petroleum products, soaps, and sugars.<sup>14</sup>

**Electrical Methods.**—Water has several unique electrical properties which permit nearly specific analyses of many liquids, solids, and gases. The most commonly employed are measurements of dielectric constant or capacitance, conductance or resistance, and electrolysis. Commercial instruments are available for making these rapid measurements.

**Dielectric Constant.**—Water has a very high dielectric constant of about 80, as compared to that of most other materials, e.g., the constant for paper is about 2.5.

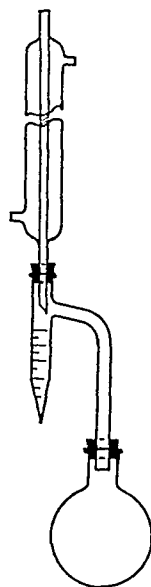


FIG. 21-1. Dean-Stark Distillation Apparatus for Determining Water in Petroleum Products.<sup>11,12</sup>

<sup>11</sup> ASTM Standards, Pt. 4, 1958, p. 1079. ASTM D95-58.

<sup>12</sup> ASTM Standards, Pt. 7, 1958, p. 1339. ASTM E123-56T.

<sup>13</sup> Dean, E. W., and Stark, D. D., Ind. Eng. Chem., 12, 486, 1920.

<sup>14</sup> Fetzer, W. R., Anal. Chem., 23, 1062, 1951.

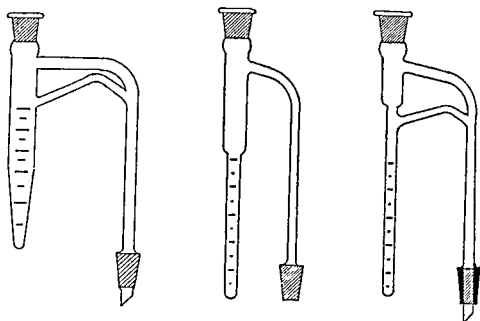


FIG. 21-2. Receivers for Use with Carriers Lighter Than Water.<sup>14</sup> *Left*—Modified Dean Stark Trap; *Middle*—Bidwell-Sterling Trap; *Right*—Modified Bidwell-Sterling Trap.

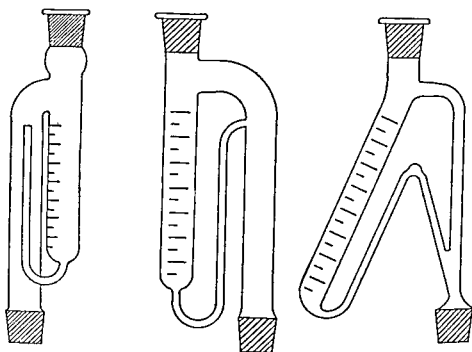


FIG. 21-3. Receivers for Use with Carriers Heavier Than Water.<sup>14</sup> *Left*—Hercules Trap; *Middle*—Langeland-Pratt Trap; *Right*—Angle Trap.

Actually, most instruments basically measure the capacitance of a condenser using the sample as a dielectric. The capacitance of a parallel plate condenser is proportional to the area of the plates and the dielectric constant of the sample between the plates and inversely proportional to the distance between the plates. Once a system is calibrated, measurements then are proportional to water content, provided conditions are reproduced. The method is in wide use for measuring water in paper, textiles, and tobacco.<sup>15</sup>

**Conductivity, Resistance.**—Conductivity (or resistance) measurements can be made conveniently on systems containing an electrolyte in which components other than water are essentially nonconducting. When electrodes at a fixed potential are placed in the sample, the current is proportional to water content. Each system must be calibrated. Instruments have been described for direct determination of water in materials such as grains, paper, textiles, plastics, tobacco, sand, wood, leather, and soils.<sup>15</sup>

In addition to determining water in solids and liquids, water in gases can be measured indirectly. Moisture in the gas is absorbed on a suitable solid, e.g., lithium salt, sulfuric or phosphoric acid, where the change in conductivity is measured.<sup>16</sup> The procedure has been applied to analyses of air, oxygen, nitrogen, and natural gas.

**Electrolysis.**—Moisture in the gas is absorbed by a suitable hygroscopic material, e.g., phosphorus pentoxide. Then the collected water is electrolyzed to oxygen and hydrogen, the electrolysis current being proportional to water content.<sup>17</sup> Commercial instruments are available for use as continuous or batch analyzers.

The technique is most useful for determining 1 to 1000 p. p. m. water in gases, such as air, nitrogen, hydrogen, carbon dioxide, argon, helium, hydrocarbons, and fluorinated hydrocarbons. Most acidic and basic materials interfere.

**Dew Point.**—The dew point is defined as the temperature at which a gas becomes saturated with moisture, i.e., where dew begins to form. Usually a mirror or highly polished metal surface is exposed to the gas in a closed system. Provision is made for cooling or heating the surface to permit alternating adjustments to slightly above or below the dew point.<sup>18</sup> The technique is suitable for analyses of inert gases which do not contain materials other than water that would condense at the dew point. Tables are available for converting dew-point temperatures to moisture contents of several gases.<sup>19</sup>

**Hygrometry.**—Relative humidities of air are usually determined with the dry- and wet-bulb psychrometer. In its simplest form, the psychrometer consists of two thermometers; the bulb of one is left bare while the other is covered by a moistened wick. Relationships have been derived relating relative humidity to the two temperatures observed after swinging the thermometers.<sup>20</sup> The wet-bulb temperature depends on rate of evaporation of water from the wick which in turn is related to moisture concentration of the air.

Variations in equipment include the "hygroscope."<sup>20</sup> This compact unit is

<sup>15</sup> Mitchell, J., Jr., in *Treatise on Analytical Chemistry*, Pt. II, Vol. I (eds. I. M. Kolthoff and P. J. Elving), Interscience Publishers, Inc., New York, 1961.

<sup>16</sup> Weaver, E. R., Hughes, E. E., and Diniak, A. W., *J. Research Natl. Bur. Standards*, 60, 489, 1958.

<sup>17</sup> Keidel, F. A., U. S. Patent 2,830,945, 1958; *Anal. Chem.*, 31, 2043, 1959.

<sup>18</sup> ASTM Standards, Pt. 8, 1958, p. 1235. ASTM D1142-58.

<sup>19</sup> Ilfield, R. M., *Anal. Chem.*, 23, 1086, 1951.

<sup>20</sup> Wexler, A., and Brombacher, W. G., *Natl. Bureau Standards Circ.* 512, 1951.

commonly called the hair hygrometer because its response depends on the behavior of human hairs kept under tension. A simple lever system connects their midpoint with a pointer. Changes in humidity cause variations in tension which are indicated directly.

Hygrometer methods are used widely in meteorology, by the air conditioning and refrigerating industries and for determining equilibrium humidities over non-volatile liquids and solids.

**Infrared Spectrophotometry.**—Absorption in both the near infrared and fundamental regions forms the basis for rapid, nondestructive determinations of water in many solids, liquids, and gases. The most useful analytical wavelengths are 1, 1.423, 1.9, 2.7, and 6 microns. In the absence of interfering materials, such as alcohols and primary or secondary amines, absorbance is proportional to concentration of water in the sample.

Applications include analyses for water in various organic compounds at 1 micron, in fuming nitric acid at 1.423 microns, in glycerol, plastics, sulfur dioxide, and hydrazine at 1.9 microns, in fluorocarbons, mercaptans and pyridine in the 2.7-micron region, and in hydrocarbons and chlorine in the 6-micron region.<sup>21</sup> The infrared method is best suited for determining water in concentrations ranging from parts per million to a few per cent.

**Nuclear Magnetic Resonance Spectroscopy.**—Instrumentation proposed measures proton resonance of the granular solid sample.<sup>22, 23</sup> The method is essentially specific for water, provided no other hydrogen-rich compounds are present in the liquid phase. Under these conditions, a sharp proton signal is given by the water superimposed on a broad signal from the solid.

The NMR technique has been used for determining several per cent water in materials such as egg albumin, candy, starches, paperboard pulp, and wood pulp.<sup>21</sup> Commercial instruments are available.

**Neutron Scattering.**—Hydrogen reduces the speed of fast neutrons more effectively than other common elements. In the absence of significant amounts of hydrogen-containing compounds other than water, this principle can be used for analysis. Application to rapid determination of water in soil has been studied extensively.<sup>24</sup> Compact field units have been developed containing a mixture of polonium and beryllium as a fast neutron source and boron trifluoride as a neutron counter.<sup>24</sup> Measurements have been made directly in the field, after lowering the source and counter in a hole drilled in the soil. The method is unaffected by temperature, texture, composition, or compaction.<sup>24</sup> Commercial apparatus also has been used on other granular solids such as cement.

**Gas Chromatography.**—Usually, during separation by gas chromatography, the water peak tends to be broad with significant tailing.<sup>25</sup> However, with continued development the technique promises to provide rapid, reliable determinations of moisture in gases.

<sup>21</sup> Mitchell, J., Jr., in *Treatise on Analytical Chemistry*, Pt. II, Vol. I (Eds. I. M. Kolthoff and P. J. Elving), Interscience Publishers, Inc., New York, 1961.

<sup>22</sup> Shaw, T. M., Elskén, R. H., and Kunsman, C. H., *J. Assoc. Official Agr. Chemists*, **36**, 1070, 1953.

<sup>23</sup> Shaw, T. M., and Elskén, R. H., *Anal. Chem.*, **27**, 1983, 1955.

<sup>24</sup> Gardner, W., and Kirkham, D., *Soil Science*, **73**, 391, 1952.

<sup>25</sup> Dal Nogare, S., and Sufianski, L. W., in *Organic Analysis*, Vol. 4 (Eds. J. Mitchell, Jr., I. M. Kolthoff, E. S. Proskauer and A. Weissberger), Interscience Publishers, Inc., New York, 1960, p. 91.

*Part II*

**SPECIAL TECHNIQUES FOR  
INDUSTRIAL PRODUCTS AND  
OTHER SPECIAL SUBSTANCES**

## Chapter 22

# COMMERCIAL ACIDS AND BASES \*

By E. F. Joy and A. J. Barnard, Jr.

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Phillipsburg, N. J.

Today, the mineral acids and common inorganic bases receive most extensive and diversified application through the full spectrum of science and technology. Their analysis is of significant interest not only to the relevant chemical producers, but also to many consuming industries. In this chapter, the analysis of these important chemicals is considered, as well as that of some additional acids that are receiving increasing tonnage application, such as perchloric, hydrofluoric, and certain organic acids. The procedures for the analysis of sulfuric acid are treated in greater detail, and often the analogous determinations for other acids can be considered as modifications of these procedures.

### DETERMINATION OF SPECIFIC GRAVITY VIA A HYDROMETER

The strength of some common acids and bases is often estimated within production plants and consuming industries by means of a hydrometer. Hydrometers of limited range are to be preferred and are best checked occasionally against standards established by the use of a pycnometer or against a set of calibrated hydrometers.<sup>1</sup> Further, the thermometer used to determine the temperature of the liquid should also be checked against standard thermometers. Specific gravity tables for some common acids and bases are given on pp. 612 through 626.

The following precautions in the use of a hydrometer are noteworthy: (1) the hydrometer should be clean and dry and at the temperature of the liquid prior to immersion; (2) the vessel should allow the hydrometer to float freely (at least  $\frac{3}{8}$  in. greater in diameter than the hydrometer bulb); (3) the hydrometer should be slowly immersed in the liquid slightly beyond the point at which it floats, and should then be allowed to float freely, (4) no air bubbles should be present in the liquid or clinging to the instrument or vessel walls; (5) the eye should be

\* Compiled with the assistance of the following companies that kindly provided recommended procedures: Allied Chem. Corp., General Chem. Div. and Solvay Process Div.; J. T. Baker Chem. Co.; Columbia Southern Chem. Co.; The Dow Chem. Co.; E. I. DuPont de Nemours & Co., Inc.; Miles Chem. Co.; Monsanto Chem. Co.; Charles Pfizer & Co., Inc.; and U. S. I. Chemicals Co. Additional information was gleaned from reports of the Tennessee Valley Authority, the United Kingdom Atomic Energy Authority, and the United States Bureau of Standards.

<sup>1</sup> Information on the correct use of hydrometers appears in United States Bureau of Standards Circular No. 57. Additional information may be secured from ASTM Standards, E100 and E126.

placed below the plane of the surface and be slowly raised until the surface, seen as an ellipse, becomes a straight line (the point at which this line intersects the hydrometer scale should be taken as the reading); (6) where the required accuracy demands, the temperature of the liquid should be taken before and after the reading, and a correction should be applied for the variation in temperature from the standard conditions for the hydrometer used and the density tables available.

In the United States, the specific gravity (and the related special units) is generally expressed at exactly 60°F. (15.56°C.), as compared to gas-free water at exactly 60°F. Under these conditions the following conversion formulas apply (and were used in the calculation of the tables on pp. 612 through 626, unless otherwise stated).

For liquids heavier than water:

$$\begin{aligned}\text{degrees Twaddell} &= (\text{sp. gr.} - 1) \times 200 \\ \text{sp. gr.} &= (\text{degrees Twaddell} + 200)/200 \\ \text{degrees Baumé, Heavy} &= 145 - (145/\text{sp. gr.})\end{aligned}$$

For liquids lighter than water: <sup>2</sup>

$$\begin{aligned}\text{degrees Baumé, light} &= (140/\text{sp. gr.}) - 130 \\ \text{sp. gr.} &= 140/(130 + \text{degrees Baumé, light})\end{aligned}$$

The inherent error in measurements with hydrometers is of the order of  $\pm 1$  in the third decimal place. The Westphal balance can be made somewhat more accurate, possibly to  $\pm 2$  in the fourth decimal place; the conventional plummet for this instrument, however, is not resistant to strong acids or alkalis. The pycnometer gives most accurate measurements of density, although its use is tedious; for the precision assay of common acids and bases, acid-base titration methods are usually preferred.

## METHODS OF MEASURING SAMPLES OF ACIDS BY WEIGHT AND VOLUME

As the prelude to the determination of the acid content of acid solutions, it is necessary to take a known weight. Special techniques are demanded where the acid is volatile or fuming, in order to assure its confinement during the weighing operations and until it is mixed with water (or standard base). Where a sample of the acid is required for the determination of an impurity, the sample is often established by taking a known volume of the acid by a pipet or from a buret. The weight of this volume may be calculated with sufficient accuracy from the specific gravity, determined either by use of a hydrometer or calculated from the estimated strength of the acid and a specific gravity-composition table:

$$(\text{volume taken}) \times (\text{sp. gr.}) = \text{weight taken.}$$

Where a number of impurities must be determined following dilution of samples with water, it is sometimes expedient to weigh a single sample of the acid, dilute to known volume with water, and employ portions of this solution in the individual determinations.

<sup>2</sup> The existence of a further Baumé scale for liquids lighter than water employed in the U. S. petroleum industry should be appreciated: API degrees Baumé = API gravity, degrees =  $(141.5/\text{sp. gr.}) - 131.5$ .



**Weighing of Dilute, Nonvolatile Acids.**—The weighing may be effected directly into a small beaker or flask, or by use of a weighing bottle or tube. The special weighing tubes for volatile acids are, of course, also satisfactory (see below). If the acid sample is to be used in the determination of the acid content, the weight taken should correspond to the optimum volume of standard base that can be delivered in a single filling of the buret used.<sup>3</sup> Hence, it is often necessary to calculate the approximate volume of the acid to be taken in order to secure a proper sample weight. Where the specific gravity of the acid has been determined by a hydrometer, the following formula may be applied:

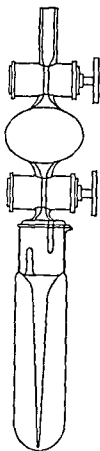


FIG. 22-1. Lunge-Rey Pipet (After Lunge, G., and Rey, H., Z. Angew. Chem., 4, 165, 1891).

$$V_a = \frac{V_b \times N_b \times M}{P_a \times D_a \times n \times 10}$$

where  $V_a$  is the milliliters of acid to be taken for weighing,  $V_b$ , the optimum milliliters of standard base to be consumed in the titration;  $N_b$ , the normality of this base;  $M$ , the formula weight of the acid;  $n$ , the number of titratable hydrogen ions furnished by one molecule of the acid ( $n = 1$  for monoprotic acids, etc.);  $P_a$ , the percentage (w/w) strength of the acid (calculated from the specific gravity by use of a proper specific gravity-composition table); and  $D_a$ , the specific gravity (determined via a hydrometer).

**Weighing of Volatile, Fuming, and Concentrated Acids.**—The application of special techniques is required.

**Lunge-Rey "Bulb-Tap" Pipet.**—This device, which is often offered commercially under the designation Lunge weighing bottle, is seen in Fig. 22-1. The acid sample is confined to the bulb between the two stopcocks. The lower part of the device is fitted with a ground glass joint and carries a protective tube; the joints are provided with a pressure-relief channel. In use, the dry device (with the tube) is weighed. The lower stopcock is closed and the upper one opened; moderate suction is applied, and the upper stopcock is then closed. The sample is then drawn into the bulb by placing the tapered tip of the lower end just below the surface of the acid, and opening the lower stopcock. This is then closed, the tip is quickly wiped,

<sup>3</sup> For the titrimetric assay of acids, the use of a chamber (or bulb) buret is recommended. Such burets, made to the specifications of the Manufacturing Chemists' Association of the United States, are commercially available, both with a 50-ml. bulb and graduated from 50 to 100 ml., and with a 75-ml. bulb and graduated from 75 to 100 ml. These burets carry a three-way stopcock. For precision titrimetry, the buret should be encased in a water jacket carrying a calibrated thermometer. Further, the buret should be connected by glass or plastic tubing, via the auxiliary stopcock lead, to the reservoir vessel containing the standard base (or acid), and also, via the top of the buret, to the same reservoir (thus furnishing a release to air of the same humidity as the solution in the buret). The closure of the reservoir vessel should also be connected, via glass tubing, to a scrubber bottle containing sodium hydroxide solution, which saturates entering air with moisture and removes  $\text{CO}_2$ . Further, a mercury relief valve from this glass tubing connection relieves any expansion of air in the reservoir due to a rise in temperature.

and the tube replaced. The increase in weight of the filled device corresponds to the sample weight. The pipet is emptied by slowly running out the acid under water, followed by thorough rinsing of the bulb chamber by the repeated addition of water through the upper stopcock with agitation.

**Dely Weighing Tube.**—This form of weighing tube, seen in Fig. 22-2, is of special interest for the routine assay of oleums and mixed acids, since it can be placed on a balance pan without auxiliary support. Satisfactory dimensions have been given by Singer.<sup>4</sup> A two-turn planar spiral, of 4-mm. I.D. glass tubing, has a total diameter of about 50 mm. and thus, a total internal capacity of about 3 ml. The spiral is terminated by lengths of 0.9-mm. I.D. capillary tubing, af-

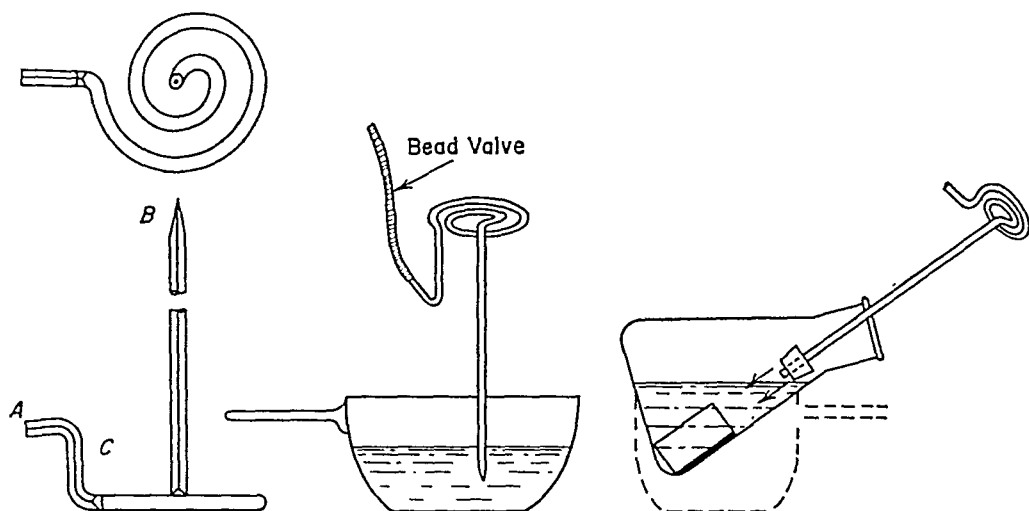


FIG. 22-2. Dely Weighing Tube, Design and Operation, Alone and with Protective Adapter.

fixed at right angles to the plane of the spiral. The central exit tube is about 155 mm. long and has a tapered tip *B*. The other exit tube carries a right angle bend *C*, directed away from the spiral, at a distance of about 30 mm. from the plane of the spiral. The end of this tube *A* may carry a ridge.

In use, the clean and dry Dely tube is weighed. Suction is applied with a rubber suction bulb attached to *A*, and the required amount of acid is drawn through tip *B*. (The satisfactory sample volume is best indicated by a permanent mark on the glass tubing.) The Dely tube is inverted, tip *B* is wiped, and the tube and sample weighed. The device is inclined so that the acid runs back into the crook *C* (to a point that may be marked on the tube wall), in order to expel as much air as possible from this end. A rubber tube, filled with water and fitted with a glass-bead valve, is attached to *A*; the other end of this tube is connected to a bottle containing water. The Dely tube is now inverted, as shown in the center illustration of Fig. 22-2, the tip being immersed in 150 to 200 ml. of cold water in a 4-in. casserole or a conical flask, depending on which vessel is to be used in the subsequent titration. By pressing the bead, water is slowly admitted to

<sup>4</sup> Singer, M. R., in *The Manufacture of Sulfuric Acid*, Duecker, W. W., and West, J. R., Eds., Reinhold Publishing Corp., New York, 1959, 419.

the tube, forcing the acid from it. Before expelling the last half-inch of acid, the rubber tube is disconnected at its attachment to the water bottle and the weak acid from the receiver is drawn back two or three in. into the Dely tube by suction provided by a rubber bulb. The acid is again almost entirely expelled by water from the bottle, and this rinsing procedure is repeated. (This step is mandatory to assure complete absorption of sulfur trioxide in the case of fuming sulfuric acid.)

Matviak<sup>5</sup> finds even with careful back-washing some sulfur trioxide may escape absorption. He recommends the attachment via a half-section cut from a rubber stopper of an adapter consisting of fire-polished glass tubing about 4.5 cm. in length and 2 cm. in diameter. As seen in the right illustration of Fig. 22-2, the Dely tube with the stopper in place is inverted and inserted quickly into the adapter, which is already immersed in the absorbing water in a conical flask. The Dely tube is rinsed repeatedly by the passage of water, and the adapter is only removed when the air space in it is completely free of mist.

The Dely tube, after use, is washed first with alcohol and then with ether; it may then be dried on an asbestos mat placed on a hot plate while clean, oil free, dry air is passed through it.

Since the loss of even traces of the acid (especially where an oleum sample is being transferred) is serious, it may be expedient, in the use of the Dely tube, to add a drop or two of phenolphthalein indicator solution to the water in the reservoir, and also the minimum amount of a very dilute sodium hydroxide solution required to elicit a faint pink color. As long as the water leaving the Dely tube is decolorized, acid is still present.<sup>6</sup>

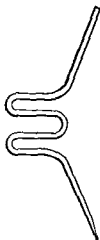


FIG 22-3. Snake Weighing Tube.

**Snake Weighing Tube.**—This simple device is easily fashioned from a 25-cm. length of 8-mm. tubing. As shown in Fig. 22-3, the tube has a double bend, on which it rests. The ends are inclined from the plane of the bends to prevent the outflow of acid; one end is drawn to capillarity. The acid is taken into the clean, dry, weighed tube, by means of suction, through an attached rubber tube and bulb. The capillary tip is wiped dry and the tube and its contents weighed. The acid is run slowly through the tip into 150 ml. of water in a casserole or conical flask with motion of the tube or the absorbing water to prevent local overheating. ("Kicking-back" of the acid indicates that the bore of the tip is too large.) The tube is then rinsed by repeatedly sucking up the solution from the receiver and expelling, and finally by passage of water.

**Bulbs and Ampoules.**—Thin-walled, pear- or globe-shaped bulbs with long stems blown from 6-mm. soft glass tubing, as well as commercial flat-bottom, long tip ampoules, are useful for weighing fuming acids (and their use is mandatory in certain thermometric methods of assay). The stem of the weighed bulb or ampoule is inserted through a hole in a small sheet of asbestos or even cardboard, which serves as a heat shield, and gently warmed over a micro flame. The tip is then quickly inserted into the acid well below its surface. When a sufficient sample has

<sup>5</sup> Matviak, M., *Chemist-Analyst*, 42, 44, 1953.  
<sup>6</sup> Suggestion, staff, General Chem. Div., Allied Chem. Corp.

been thus obtained, the tip is withdrawn, quickly wiped, and sealed over the flame (without loss of glass!). The sealed bulb or ampoule is wiped clean and dry, and reweighed. (Where conditions permit, the ampoule may alternatively be filled by a pipetting operation.) The filled and sealed ampoule or bulb, after weighing, is transferred to the absorbing liquid (water or a sodium hydroxide solution) in a thick-walled vessel and is broken by pressure from a heavy stirring rod with a flattened end or by vigorous agitation (e.g., if a glass-stoppered conical flask or bottle is used).

**Other Weighing Devices.**—Obviously other techniques and devices may be applied to the establishment of a weighed sample of acid under confined conditions. The use of a weighing buret is sometimes appropriate, and the design of Friedman and LaMer,<sup>7</sup> which is commercially available, is noteworthy. For use with fuming acids, such a buret may be fitted with a long, thin-bore delivery tube, as earlier suggested by Blay and Burkhard (Fig. 22-4). The latter is graduated in half-milliliter divisions from 0 to 20 ml.; a half-sized apparatus is used for oleum where a 2-ml. sample suffices for a determination. The delivery tube, *E*, is placed in the tube during the titration; the stopper, *A*, is vented. W. W. Scott suggested replacing the simple glass stopper of the Blay-Burkhard design by a crook-bored stopper carrying a capillary tube extension (*A'* in Fig. 22-4). The vent to the air is opened or closed by a slight turn of this stopper, thus providing alignment with a channel. By means of this tube, acid may be drawn into the buret according to the Lunge-Rey pipet procedure, above, to allow filling from the bottom; thus avoiding any pouring or intermediate transfer of the acid.

Conventional weighing bottles may often be used with even concentrated non-fuming acids, by the expedient of placing the weighing bottle and its loosened stopper with the acid sample well under the surface of the absorbing water (or base).

## SULFURIC ACID

Sulfuric acid,  $\text{H}_2\text{SO}_4$ , made by the contact process, is relatively pure and may be obtained in any required strength from dilute solutions to 'oleums' ("fuming" acid). The principal strengths offered in the United States include 60° Baumé, Heavy (77.67%  $\text{H}_2\text{SO}_4$ ),<sup>8</sup> 66° Baumé, Heavy (93.19%  $\text{H}_2\text{SO}_4$ , Oil of Vitriol), and

<sup>7</sup> Friedman, H. B., and LaMer, V. K., *Ind. Eng. Chem., Anal. Ed.*, 2, 54, 1930.

<sup>8</sup> The nominal 60° Baumé, Heavy acid actually shipped in winter months may be 59.8–60.0° Baumé, Heavy, to prevent its freezing.

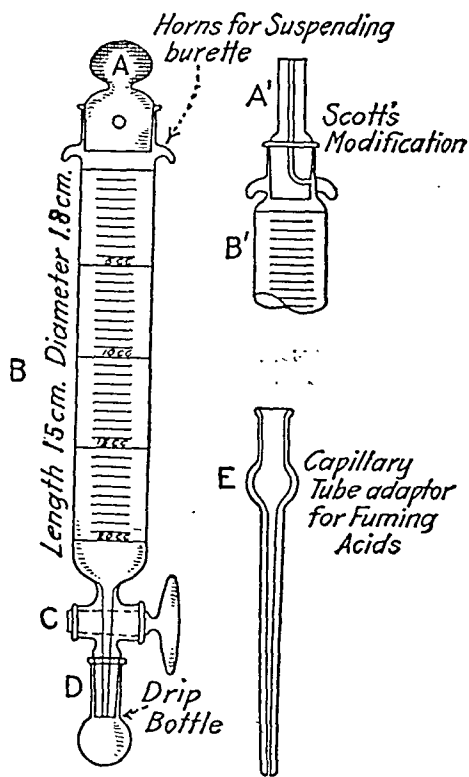


FIG. 22-4. Blay-Burkhard Graduated Weighing Buret and Scott's Modification.

97%  $\text{H}_2\text{SO}_4$ . (Oleum and "mixed acid" are considered in later sections of this chapter.) Dilute sulfuric acid solutions ranging in strength from 27.88% to 93.19%  $\text{H}_2\text{SO}_4$  (sp. gr. 1.205 to 1.835) are available, to some extent on a custom basis, for use as battery electrolytes. In *National Formulary X*, sulfuric acid (94–95%  $\text{H}_2\text{SO}_4$ ) and dilute sulfuric acid (9.5 to 10.5 g. of  $\text{H}_2\text{SO}_4$  per 100 ml.) had official drug status in the United States, but these entries were deleted from *National Formulary XI*. Reagent grade sulfuric acid, meeting American Chemical Society specifications, has a strength of 95.0–98.0%  $\text{H}_2\text{SO}_4$ ; the typical product marketed has a strength of 96.0%  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84). Some composition data for sulfuric acid are given in the tables on pp. 613 through 616. For further and more extensive physico-chemical data, the monograph of Duecker and West should be consulted.<sup>9</sup>

### SULFURIC ACID CONTENT

**Sulfuric Acid Content by Specific Gravity.**—The specific gravity of sulfuric acid increases with its concentration up to a maximum of 1.8439 at 97.50%  $\text{H}_2\text{SO}_4$ ; above this concentration the specific gravity decreases to a value of 1.8391 at 100.0%  $\text{H}_2\text{SO}_4$ . However, the change in specific gravity with increasing composition is not very marked above 93.19% (corresponding to sp. gr. 1.8354), and, hence, hydrometer measurements are not recommended above this value. Specific gravity-concentration tables for sulfuric acid appear on pp. 613 through 616. For internal plant control of sulfuric acid in the range 93–100%  $\text{H}_2\text{SO}_4$ , a dilution and a hydrometer measurement is often performed ("Dilution Test"). Usually the sample of strong acid is diluted, under good cooling, with an equal quantity of water. From the specific gravity of the resulting dilute solution, the acid content of the original acid can be estimated from composition tables.

**Sulfuric Acid Content by Alkalimetric Titration. Procedure.**—By means of a suitable technique (see "Weighing of Volatile, Fuming, and Concentrated Acids," above) weigh a sample of  $\text{H}_2\text{SO}_4$  (equivalent to 4.0 to 4.7 g. of 100%  $\text{H}_2\text{SO}_4$  if a chamber buret is used, and hence, the volume of 1 N NaOH consumed will be in the range 80 to 95 ml) and transfer to a 110-mm. diameter (#4) porcelain casserole, containing 150 ml. of freshly boiled and cooled ( $\text{CO}_2$ -free) water. Add 1 ml. of 1% phenolphthalein solution, and titrate to a permanent faint pink color with  $\text{CO}_2$ -free 1 N NaOH, which has been standardized to the phenolphthalein end point, and which, before the titration, has been brought to constant temperature. Allow the (chamber) buret to drain and read the volume of NaOH delivered. Note the temperature of the NaOH solution, and add a correction of 0.00032 ml. per milliliter of 1 N NaOH added for each degree Centigrade below its standardization temperature; or subtract the correction for each degree above.

**Remarks.**—The use of a chamber buret is described in footnote 3, p. 536. Some workers, especially for rapid, routine analysis, prefer to dilute an appropriate sample of the acid to known volume (usually 1000 ml.) with  $\text{CO}_2$ -free water, and to use 100 ml. (taken with a pipet or volumetric flask calibrated "to deliver") for the titration of the total acidity, and further aliquots for other required determinations (e.g., see the remarks on p. 535). In such a procedure 0.3333 . . . N NaOH is useful (temperature correction, 0.00025 ml. per milliliter of base per degree

<sup>9</sup> Duecker, W. W., and West, J. R., eds., *The Manufacture of Sulfuric Acid*, Reinhold Publishing Corp., New York, 1959, especially pp. 434–471.

Centigrade). Methyl orange or methyl red may be preferred as the indicator, and both indicators may be used in sequence, i.e., titrating to the orange-yellow of methyl orange, then adding methyl red, and titrating dropwise to a sharp end point marked by a color change of red to canary yellow. Where these indicators are used, the possible need for a correction for the carbonate content of the base should be noted. Some workers prefer bromphenol blue as the indicator. If phenolphthalein is used, any sulfur dioxide present is titrated as a dibasic acid; the calculation factors usually given are based on this assumption. With highly colored samples ("black" acid), 5 ml. of phenolphthalein indicator may be added, and the end point color change observed in the foam above the vigorously agitated solution. A more expeditious and generally applicable approach is the use of a potentiometric end point employing a pH-meter and titrating to the pH of the end point in the standardization process for the base. Where the acid contains significant amounts of volatile acids or nitrogen oxides, they may be removed by partial evaporation of the sample (see determination of sulfuric acid in mixed acid, p. 555), or a correction should be applied following the determination of the acidic impurities (see below under "Calculations").

#### Calculations.

% Total Acidity as  $\text{H}_2\text{SO}_4$

$$= \frac{(\text{milliliters of NaOH}) \times (\text{normality of NaOH}) \times 0.049039 \times 100}{\text{sample weight in grams}},$$

where the volume of NaOH is corrected for temperature.

If the sample contains a significant amount of other acids, a correction may be applied following their separate determination. For example,

$$\% \text{H}_2\text{SO}_4 = \% \text{Total Acidity as H}_2\text{SO}_4 - (\% \text{HNO}_3 \times 0.7782) - (\% \text{HCl} \times 1.345).$$

**Other Methods for Determining the Sulfuric Acid Content.**—Fialko and Kostromitin described the application of conductivity measurements for the determination of sulfuric acid.<sup>10</sup> Singer has given cell specifications and a wiring diagram for the application of this method to 97.5 to 99.7%  $\text{H}_2\text{SO}_4$ .<sup>11</sup> However, strict control of temperature and calibration is necessary, and variations in impurities introduce significant errors. The method appears more useful for in-plant control. Zimmerman and Brandt and Langmyhr and Skaar<sup>12</sup> have described spectrophotometric methods for the determination, respectively, of 85 to 99% and 80 to 99.5%  $\text{H}_2\text{SO}_4$  employing quinalizarin and 1,1'-dianthrimide as the chromogenic agents.

For sulfuric acid of 95.5–100.0% strength, thermometric methods of assay are applicable (see further under "Oleum," p. 554).

<sup>10</sup> Fialko, G. M., and Kostromitin, L. A., *Zavodskaya Lab.*, 16, 1268, 1950; *C. A.*, 47, 3188, 1953.

<sup>11</sup> Singer, M. R., in *Manufacture of Sulfuric Acid*, Duecker, W. W., and West, J. R., eds., Reinhold Publishing Corp., New York, 1959, 424–425.

<sup>12</sup> Zimmerman, E., and Brandt, W. W., *Talanta*, 1, 374, 1958; Langmyhr, F. J., and Skaar, O. B., *Anal. Chim. Acta*, 23, 28, 1960.

### DETERMINATION OF RESIDUE ON IGNITION FOR SULFURIC ACID

The determination of the residue on ignition (that is, on heating) is routinely conducted in the analysis of sulfuric acid of all grades. The residue is largely iron(III) oxide. Crude acid, especially chamber acid, may present considerable residue, including substances entering from the sulfur ore.

**Procedure.**—Weigh 50 to 100 ml. of the  $H_2SO_4$  into a tared platinum or silica dish. In a hood, evaporate to dryness by gentle heating, and then ignite to a red heat for about 5 min. When no more fumes evolve, allow the dish to cool and re-weigh it. The difference between the final weight and the tare weight corresponds to the weight of the residue.

**Calculation.**

$$\% \text{ Residue on Ignition} = \frac{[(\text{final dish weight}) - (\text{tare dish weight})] \times 100}{\text{sample weight}}$$

### DETERMINATION OF HYDROCHLORIC ACID IN SULFURIC ACID

Where the sulfuric acid contains only small amounts of hydrochloric acid, the estimation of the latter may be based on the matching of the turbidity produced in the sample by the addition of silver nitrate with that produced in a blank containing a known amount of sodium chloride. Large amounts of hydrochloric acid may be determined by dilution of the acid to about 20% and application of a conventional Volhard titration (see Vol. I, p. 329).

**Turbidimetric Determination of Small Amounts of Hydrochloric Acid. Procedure.**—Into 50 ml. of (chloride-free) water, pour a sample of  $H_2SO_4$  containing 0.0001 to 0.001 g. of HCl, while cooling in a cold water bath. When the solution has cooled to room temperature, transfer to a 100-ml. low-form Nessler tube, and dilute to about 90 ml. Prepare a blank by adding to 50 ml. of the water an equivalent amount of chloride-free (reagent grade)  $H_2SO_4$ . Cool and transfer to a second Nessler tube and dilute to about 90 ml. To each tube add 5.0 ml. of 1%  $AgNO_3$  solution, and gently mix the contents of each with a ring stirrer. (Avoid vigorous stirring which will lead to coagulation and reduction in turbidity, and hence low results.) From a buret add a standard NaCl solution (0.1603 g. reagent grade NaCl dissolved and diluted to 1000 ml. with chloride-free water) until the turbidity almost matches that of the sample. Dilute the contents of both tubes to 100 ml. with water, and continue the addition of NaCl to the blank until the turbidities match closely when observed against a black background with lateral illumination.

**Calculation.**

$$\% \text{ HCl} = \frac{(\text{milliliters of NaCl solution}) \times 0.00010 \times 100}{\text{sample weight in grams}}$$

**Remarks.**—Some workers prefer to carry out a preliminary determination and then to use freshly prepared standards and sample for the actual determination.

Alternatively, the result may be expressed as percentage of chloride.

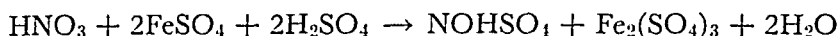
DETERMINATION OF HYDROFLUORIC ACID IN  
SULFURIC ACID

Traces of hydrofluoric acid in sulfuric acid may be determined by the method of Williard and Winter, a double distillation approach being preferred. (See Vol. I, pp. 432-433.)

## DETERMINATION OF NITRIC ACID IN SULFURIC ACID

The approach adopted for the determination of nitric acid in sulfuric acid, which at the trace level is often termed the "determination of nitrogen compounds," depends on the level encountered in the sample and grade. In the case of "mixed acid" containing substantial amounts of nitric acid, a titration with iron(II) sulfate to the appearance of the brown-colored iron-nitroso complex is feasible.<sup>13</sup> Trace amounts of nitric acid may be determined colorimetrically via formation of this same complex, or with brucine as the chromogenic agent.

*Titrimetric Iron(II) Sulfate Method for Nitric Acid in Sulfuric Acid.*—This method is based on the reduction of nitrate (whether "bound" or "free") in a concentrated sulfuric acid medium with iron(II) to form nitrososulfuric acid:



When the first excess of iron(II) is added, the brown-colored iron-nitroso complex forms and signals the end point. It is operationally desirable that the nitrate concentration in the titration medium be similar to that taken for the standardization of the iron(II) sulfate reagent; this requires a preliminary titration with the sample, depending on its nitrate content, taken either as is or diluted. The iron(II) sulfate reagent is standardized by the titration of known amounts of nitric acid.

*Procedure.*—Perform a scaled-down titration after the second and third paragraphs of this procedure, with the  $\text{H}_2\text{SO}_4$  sample, thus determining the milliliters of standardized  $\text{FeSO}_4$  solution equivalent to 1 ml. of it. This requires 2 to 3 min. Now dilute a weighed portion of the sample with (nitrate-free) water so that each 10 ml. contains from 0.1 g. to 0.8 g. of  $\text{HNO}_3$ , and preferably 0.4 g. For example, suppose 1 ml. of  $\text{H}_2\text{SO}_4$  sample requires 43.8 ml. of  $\text{FeSO}_4$  solution; then 10 ml., which is the amount to be taken in the final titration, would require 438 ml. However, consumption of only 20 ml. of  $\text{FeSO}_4$  solution is desired in that titration. Hence the sample should be diluted 20:438, and conveniently 23 ml. can be diluted to 500 ml. Thus 23 ml. of sample are weighed, transferred quantitatively to a 500-ml. volumetric flask, and diluted to mark with water.

Place a 250-ml. beaker containing 100 ml. of concentrated, nitrate-free (reagent grade)  $\text{H}_2\text{SO}_4$  (93%+) in a deep vessel containing cold water. From a pipet, accurately calibrated to contain exactly 10 ml., deliver 10.0 ml. of the appropriately diluted  $\text{H}_2\text{SO}_4$  sample (see above) keeping the delivery tip below the  $\text{H}_2\text{SO}_4$  surface and in constant circular motion near the beaker sides in order to avoid local heating.

Now add  $\text{FeSO}_4$  solution (see below) from a buret in a fine stream until the yellow color that first forms takes on a faint brownish tinge i.e., becomes a dirty yellow. Now rinse the pipet by sucking up the mixture and draining it back into

<sup>13</sup> Bowman, F. C., and Scott, W. W., J. Ind. Eng. Chem., 7, 766, 1915.



the beaker. Complete the titration by adding the  $\text{FeSO}_4$  solution dropwise until the yellow-brown color reappears. (A drop in excess produces an appreciable darkening of the solution; large excess, a brown-red color; small amounts of  $\text{HNO}_3$  may yield only a red color.)

**Preparation and Standardization of Iron(II) Sulfate Solution.**—Dissolve 176.5 g. reagent grade  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in about 400 ml. of water. Add about 500 ml. of  $\text{H}_2\text{SO}_4$  (60%) i.e., 1 volume reagent grade  $\text{H}_2\text{SO}_4$  (96%) with 0.6 volume of water, with constant stirring. Dilute the cooled solution to exactly 1000 ml. with water. One ml. of this solution will be equivalent to about 0.02 g.  $\text{HNO}_3$ . Determine the exact value by running 10.0 ml. of a solution containing 10.0 g.  $\text{HNO}_3$  per 1000 ml. of solution into 100 ml. of nitrate-free  $\text{H}_2\text{SO}_4$  (93.2%) and proceeding with the  $\text{FeSO}_4$  titration after the third paragraph of the above procedure. The grams of  $\text{HNO}_3$  equivalent to 1 ml. of  $\text{FeSO}_4$  solution = (milliliters  $\text{HNO}_3$  solution taken)  $\times$  (% (w/v) of  $\text{HNO}_3$  in solution)  $\div$  [(milliliters of  $\text{FeSO}_4$  solution required) - 0.2 ml.]. (The 0.2 ml. correction corresponds empirically to the amount of  $\text{FeSO}_4$  required to produce the desired color reaction in 100 ml. of the  $\text{H}_2\text{SO}_4$  medium.)

**Calculation.**—For the sample, the percentage of  $\text{HNO}_3$  is given by:

$$\% \text{HNO}_3 = \frac{(\text{milliliters of FeSO}_4 \text{ solution required} - 0.2) \times F \times 100}{(\text{fraction of total sample used in titration}) \times (\text{sample weight in grams})}$$

where  $F$  is the grams of  $\text{HNO}_3$  equivalent to 1 ml. of the  $\text{FeSO}_4$  solution.

**Remarks.**—Samples known to contain over 10%  $\text{HNO}_3$  (mixed acid) should be diluted appropriately with reagent grade  $\text{H}_2\text{SO}_4$  to a definite volume and a 10 ml. aliquot taken in the above procedure. Bowman and Scott<sup>13</sup> established the correction as 0.2 ml. by experiment. The existence of this correction has been confirmed.<sup>14</sup> The  $\text{H}_2\text{SO}_4$  concentration is the major factor affecting its value; by performing the titration in an 86 to 91%  $\text{H}_2\text{SO}_4$  medium at a temperature not above 10°C., the blank becomes negligible. By substitution in the procedure of a potentiometric end point with a platinum-tungsten electrode pair, the correction is obviated, and the titration of colored samples is also facilitated.<sup>14</sup>

**Colorimetric Iron-Nitro Method for Nitric Acid in Sulfuric Acid.**—A procedure for the estimation of small amounts of nitric acid (and associated nitrogen compounds) in sulfuric acid may be based on the color developed on addition of iron(II) sulfate. The method is preferred by many workers over a diphenylamine procedure (see Vol. I, p. 748), better selectivity being claimed.

**Procedure.**—Into each of two 100-ml., tall form Nessler tubes, add 50–60 ml. (nitrate-free) reagent grade  $\text{H}_2\text{SO}_4$  and 5 ml. of a 10% aqueous  $\text{FeSO}_4$  solution. Mix each solution with a glass plunger and cool to 10° to 15°C. in an iced water bath. To one tube add by a pipet 10 to 25 ml. of cooled  $\text{H}_2\text{SO}_4$  sample (depending on the expected  $\text{HNO}_3$  content); dilute to 100 ml. with cooled reagent grade  $\text{H}_2\text{SO}_4$ , and mix. To the second tube add dropwise (preferably from a micro buret) a standard  $\text{KNO}_3$  solution (1 ml. equivalent to 0.0001 gram of  $\text{HNO}_3$ ) until the solution color is close to that of the first tube, and dilute to 100 ml. with cooled reagent grade  $\text{H}_2\text{SO}_4$  and mix. Now add more  $\text{KNO}_3$  dropwise, and with mixing, until the color developed matches that of the sample tube as viewed against a white background illuminated by diffuse light.

<sup>13</sup> Johnson, C. L., *Anal. Chem.*, 25, 1276, 1953; McKinney, C. D., Jr., Rogers, W. H., McNabb, W. M., *Anal. Chem.*, 19, 1041, 1947.

**Calculation.**—The percentage of  $\text{HNO}_3$ , or of nitrogen compounds expressed as  $\text{HNO}_3$ , is calculated from the milliliters of  $\text{KNO}_3$  solution added, expressed as  $\text{HNO}_3$ , and the sample weight, which is calculated from the volume and density of the sample.

**Remarks.**—The procedure is applicable only where selenium is essentially absent. The final solution should contain 0.0005 to 0.005 g. of  $\text{HNO}_3$ , and be 90 to 100% in  $\text{H}_2\text{SO}_4$ . This latter condition should be considered in the analysis of weaker concentrations of sulfuric acid. The method can be adopted for use with a filter photometer with the use of a filter transmitting in the region 525  $\text{m}\mu$ ; the result is read from a standard curve.<sup>15</sup>

**Photometric Brucine Method for Trace Nitric Acid in Sulfuric Acid.**—The yellow color produced by brucine in a sulfuric acid solution with nitrate (or nitrite) permits the photometric determination of nitric acid in sulfuric acid.<sup>16</sup>

**Procedure for 93–99%  $\text{H}_2\text{SO}_4$ .**—To 9.0 ml. of demineralized water (passed through a mixed bed of ion exchange resin) in a 125-ml. conical flask, add 1.0 ml. of brucine sulfate solution containing 0.60 g. per 100 ml. of water (the solution is stable for at least one week; brucine is quite *toxic*). Now add rapidly, and with vigorous swirling, 20.0 ml. of the  $\text{H}_2\text{SO}_4$  sample (93–99%  $\text{H}_2\text{SO}_4$ ). Allow to stand exactly 1 min., and cool in a water bath for 2 min.

Transfer the solution to a cuvet. Fill a similar cell with a cooled mixture of 10.0 ml. of water and 20.0 ml. of the  $\text{H}_2\text{SO}_4$  sample (93–99%); this serves as the blank. Measure the absorbance in a filter photometer using a blue filter. The nitric acid content of the sample can be read from an appropriate standard curve prepared with  $\text{H}_2\text{SO}_4$  of a concentration similar to that of the sample by addition of known amounts of  $\text{KNO}_3$ .

**Modified Procedure for 78%  $\text{H}_2\text{SO}_4$ .**—Pipet 1.0 ml. of the brucine sulfate solution into a 125-ml. conical flask, and add 9.0 ml. of reagent grade  $\text{H}_2\text{SO}_4$ . Now add 20.0 ml. of the  $\text{H}_2\text{SO}_4$  sample (78%) rapidly and with vigorous swirling. Heat until the temperature definitely reaches 118° but does not exceed 120°C. Then cool in a water bath for 2 min. Transfer the solution to a cuvet. Fill a second cell with a cooled mixture of 1.0 ml. of demineralized water, 9.0 ml. of reagent grade  $\text{H}_2\text{SO}_4$ , and 20.0 ml. of the  $\text{H}_2\text{SO}_4$  sample (78%). Proceed with the photometric measurement as given above. Determine the  $\text{HNO}_3$  content of the reagent grade sulfuric acid employed by the "Procedure for 93–99%  $\text{H}_2\text{SO}_4$ ," above, and correct the result appropriately for the 9 ml. used.

**Remarks.**—Nitrite (nitrosylsulfuric acid) yields about one-third the absorbance of nitrate in the brucine procedure. Nitrite may be removed by treatment of the  $\text{H}_2\text{SO}_4$  sample with sodium azide, sulfamic acid, or urea. Chlorate, hypochlorite and persulfate interfere, yielding yellow or red colors. Titanium reacts with brucine to form a pink color, and perchlorate is precipitated by this reagent.

## DETERMINATION OF SULFUROUS ACID (SULFUR DIOXIDE) IN SULFURIC ACID

Sulfur dioxide may be estimated in sulfuric acid by an iodimetric procedure.

**Procedure.**—To 300 ml. of cold water add a sample of the sulfuric acid containing 0.001 to 0.05 g. of  $\text{SO}_2$ . Add some starch indicator and titrate with standard

<sup>15</sup> Swann, M. H., and Adams, M. L., *Anal. Chem.*, **28**, 1630, 1956.

<sup>16</sup> Based on a procedure of General Chem. Div., Allied Chem. Corp.; see also Boltz, D. F., *Colorimetric Determination of Nonmetals*, Interscience Publishers, Inc., New York, 1958, 143–4 and 151–2.

0.1 *N* iodine to the first permanent blue color. Where large amounts of  $\text{SO}_2$  are present, add almost the required amount of iodine to the water before the sample.

Calculations.

$$\% \text{SO}_2 = \frac{(\text{milliliters of iodine}) \times (\text{normality of iodine}) \times 0.03203 \times 100}{\text{sample weight in grams}}$$

For the percentage of  $\text{H}_2\text{SO}_3$ , the factor is 0.04104.

Remarks.—Where the procedure is applied to a high-strength oleum (about 40% free  $\text{SO}_3$  or greater), the weighed sample should be mixed with 2.5 to 3 times its own volume of reagent grade  $\text{H}_2\text{SO}_4$  before the addition to water; a blank for this  $\text{H}_2\text{SO}_4$  is determined separately and deducted.

### DETERMINATION OF ARSENIC IN SULFURIC ACID

The determination of traces of arsenic in sulfuric acid (less than 0.005%) is usually accomplished by the Gutzeit method, a preliminary distillation being recommended where the arsenic content is less than 0.00005%. Large amounts of arsenic may be determined iodimetrically.

**Iodimetric Determination of Arsenic in Sulfuric Acid.**—Where the arsenic content of the sulfuric acid sample is greater than about 0.05%, reduction and direct titration with iodine solution is feasible. The procedure is given in Vol. I, p. 108. Where antimony is present in substantial amounts, arsenic must be previously separated by distillation as  $\text{AsCl}_3$  (see Vol. I, pp. 108 and 110).

**Trace Arsenic in Sulfuric Acid by the Gutzeit and Silver Diethyldithiocarbamate Methods.**—The Gutzeit method has long been applied to the determination of trace arsenic in sulfuric acid. The general procedure given in Vol. I, pp. 118–124, is directly applicable, with the special considerations noted on p. 122. In the use of the Gutzeit method for the purity grades of sulfuric acid, it is desirable to consult the information on this method given in *Official Methods of A. O. A. C., Reagent Chemicals*, and the *U. S. Pharmacopeia*. Precision and accuracy can only be secured in this method by maintaining as closely identical conditions as possible for each unknown, standard, and blank. The silver diethyldithiocarbamate photometric finish<sup>17</sup> to the (Gutzeit) evolution of arsine is promising as the sensitivity is high, and the standard curve is reproducible from run to run. (See Vol. I, pp. 135–137.)

### DETERMINATION OF ANTIMONY IN SULFURIC ACID

If antimony is present in significant amounts it must be separated from arsenic as a preliminary step to the Gutzeit determination of arsenic (see Vol. I, pp. 118–119). The antimony remains in the still, and may subsequently be evolved by adding zinc dissolved in concentrated hydrochloric acid. The antimony in the distillate is then determined by a modified Gutzeit method (see Vol. I, pp. 102–105). However, doubt has been cast as to whether satisfactory recoveries are obtained in the evolution of under 10  $\mu\text{g}$ . of antimony.<sup>18</sup>

<sup>17</sup> Vašák, V., and Šedivec, V., *Chem. listy*, 46, 341, 1952; *Collection Czechoslovak Chem. Commun.*, 18, 64, 1953; see also Dubois, L., and Monkman, J. L., *Am. Ind. Hygiene Assoc. J.*, 22, 292, 1961.

<sup>18</sup> See literature cited, Sandell, E. B., *Colorimetric Determination of Traces of Metals*, Interscience Publishers, Inc., New York, 3rd Ed., 1959, 257.

## DETERMINATION OF SELENIUM IN SULFURIC ACID

Large amounts of selenium are seldom encountered in sulfuric acid in the contemporary period (if they were present, they could be reduced and weighed as elemental selenium). Formerly trace selenium was determined turbidimetrically; however, the method has poor sensitivity and reproducibility. The introduction of the highly selective chromogenic agent 3,3'-diaminobenzidine has now afforded a highly satisfactory photometric procedure for selenium in sulfuric acid.<sup>19</sup>

**Photometric Determination of Selenium.**—In a 100-ml. glass-stoppered, borosilicate conical flask, dilute and neutralize the weighed  $\text{H}_2\text{SO}_4$  (1 g. of concentrated  $\text{H}_2\text{SO}_4$  or an equivalent amount of other sulfate-containing sample) with 5 *M*  $\text{NaOH}$ . Add 30 ml. of 20%  $\text{NH}_4\text{Cl}$  solution and dilute with water to 50 ml. Add 2 ml. of 2.5 *M* formic acid, and then 2 ml. of a 0.5% solution of 3,3'-diaminobenzidine (prepare this solution every few days and store in a refrigerator). If necessary, add further formic acid to adjust to pH 2 to 3. Allow the solution to stand 3 to 4 hrs. at room temperature, adjust to pH 6 to 7 with 7 *M* aqueous  $\text{NH}_3$  (about 0.5 to 0.6 ml.). Add exactly 10 ml. of toluene, and shake vigorously for 30 sec. Separate the organic phase after a few minutes, and measure the absorbance at 420  $\text{m}\mu$  against a reagent blank prepared by employing selenium-free sulfuric acid in place of the acid sample. Calculate the selenium content from a calibration curve prepared by carrying known amounts of selenium through the procedure. Beer's law is obeyed at least in the region 5 to 25  $\mu\text{g}$ . of selenium per gram of sulfuric acid. For samples extremely low in selenium, a larger sample may be taken, but a new calibration curve should be prepared since the sulfate concentration influences the color development.

**Remarks.**—At the low level, if high blanks are encountered, the trace selenium content of the toluene should be checked; further, it should be appreciated that some glass may contain sufficient selenium so that an erroneous result may be obtained.

## DETERMINATION OF LEAD IN SULFURIC ACID

Large amounts of lead, which may enter sulfuric acid through contamination, may be determined gravimetrically as lead sulfate or lead chromate. Lead in trace amounts (0.005% or less) is determined photometrically, usually by a dithizone procedure.

**Gravimetric Determination of Lead Contamination in Sulfuric Acid.**—The two common approaches to the determination of large amounts of lead in sulfuric acid follow classical procedures and need only brief description.

**Lead Sulfate Procedure.**—Dilute the weighed  $\text{H}_2\text{SO}_4$  sample (93%+) with an equal volume of water. Add to the cooled solution double its volume of ethanol. Allow to stand 2 hr. or more. Separate the  $\text{PbSO}_4$  precipitate on a tared Gooch crucible, wash with ethanol, dry, ignite to a dull red heat, and reweigh. Express the gain in weight as percentage of lead in the original sample. (See also Vol. I, p. 560.)

**Lead Chromate Procedure.**—Ignite the weighed  $\text{H}_2\text{SO}_4$  sample and extract the residue with ammonium acetate solution. Make the extract acidic with acetic acid, and precipitate  $\text{PbCrO}_4$  by addition of a slight excess of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

<sup>19</sup> Danzuka, T., and Ueno, K., *Anal. Chem.*, **30**, 1370, 1958; Cheng, K. L., *ibid.*, **28**, 1738, 1956; Cheng, K. L., *Chemist-Analyst*, **45**, 67, 1956.

Dry and weigh the separated precipitate, and express the result as percentage of lead in the original sample. (See also Vol. I, p. 562.)

**Photometric Determination of Traces of Lead in Sulfuric Acid.**—A conventional dithizone procedure is usually applied to the determination of small amounts of lead in sulfuric acid (see Vol. I, pp. 569–572 and 610–612). Often a volume of the (concentrated) sulfuric acid sample containing 10 to 70  $\mu\text{g}$ . of lead is pipetted into 50 ml. of water and the resulting solution (or an aliquot) is used in the dithizone procedure. For a high purity acid or an oleum, a sufficiently large sample to provide a similar amount of lead is fumed to a volume of about 5 ml. (this also removes excessive amounts of sulfate); after cooling, the concentrate is added slowly and with continual stirring to 50 ml. of water. Highly colored (black) acid or oleum should be reduced initially to fumes with the addition of crystals of potassium nitrate until the color is discharged. If lead sulfate precipitates on the direct dilution of a sulfuric acid, a smaller sample or a further dilution should be employed, or an initial fuming step.

### DETERMINATION OF "HEAVY METALS" IN SULFURIC ACID

In the manufacture of high purity grades and pharmaceutical grade mineral acids (bases, and salts), a so-called "heavy metals" method has long been applied, either as a limit test, or a turbidimetric determination. In the usual meaning, the term "heavy metals" here denotes the precipitation of the metals of the hydrogen sulfide group under specified conditions (now often acetate medium, pH 3 to 4) and expression of the result in terms of the equivalent amount of lead that gives the same result in the test or determination.

**Procedure.**<sup>20</sup>—Weigh an appropriate sample (20 g.) of  $\text{H}_2\text{SO}_4$  (or other mineral acid) containing 0.01 to 0.05 mg. of "heavy metals" into a dish or beaker. Add 10 mg. of anhydrous  $\text{Na}_2\text{CO}_3$  dissolved in a little water, and evaporate almost to dryness. Then add 1 ml. of concentrated  $\text{HNO}_3$  and evaporate to dryness. Take up the residue in 20 ml. of metal-free water, add 1 drop of phenolphthalein indicator solution and neutralize with 1 *N* NaOH. Add 1 ml. of 1 *N* acetic acid and 10 ml. of freshly saturated  $\text{H}_2\text{S}$  water, and dilute to 40 ml. with water. Compare the color developed with that of standards containing 0 to 0.05 mg. of lead (as the nitrate salt) and the same quantities of reagents as the sample residue. As a photometric procedure compare the unknowns and standards against water using a blue filter. Express the result as

$$\% \text{ Heavy Metals as Lead} = \frac{(\text{milligrams of Pb in standard matching the sample}) \times 0.10}{\text{sample weight in grams}}$$

**Remarks.**—Various heavy metals tests and determinations have been described employing, for example, sulfide precipitation from an ammoniacal tartrate medium or an extraction (with dithizone). Possibly the results of such methods should be so designated so as to differentiate them from the classical "heavy metals" procedures. With process liquors containing large amounts of inert salts, it may be necessary to add a similar concentration of salts to the standards to obtain meaningful results. Further, in the general concept of the test, where the color shade (not intensity) developed by the unknown departs markedly from that of the lead

<sup>20</sup> For modification of this procedure for diverse substances and solutions, see entries, U. S. Pharmacopeia and American Chemical Society, Reagent Chemicals—1960, Washington, D. C., 1961.

standards, it is appropriate to employ standards based on addition of lead to a solution of the sample.

### DETERMINATION OF IRON IN SULFURIC ACID

Iron in large amounts in sulfuric acid (i.e., 0.02% or more) is usually determined via classical separation as iron(III) hydroxide, re-solution in hydrochloric acid, reduction with tin(II) chloride, and titration with potassium dichromate to the diphenylamine or barium diphenylaminesulfonate end point (see Vol. I, pp. 542–544). If antimony or arsenic is present in substantial amounts, they are removed by a prior acid sulfide separation. Trace amounts of iron are determined by a colorimetric thiocyanate procedure.

*Determination of Trace Iron in Sulfuric Acid.*—The classical thiocyanate colorimetric method for iron(III) is commonly employed (see Vol. I, p. 552). Visual comparison or a filter photometer may be applied, depending on the sensitivity required.

*Visual Comparison Procedure.*—Add a weighed  $\text{H}_2\text{SO}_4$  sample (about 5 g.) to 10 ml. of water in a small beaker. (If any iron or iron-containing dust is in suspension, heat to dissolve it.) Pour the cooled solution into a 100-ml. Nessler tube with water-rinses. Add 0.1 *N*  $\text{KMnO}_4$  dropwise to the appearance of a faint red color, and then 10 ml. of a 10% aqueous  $\text{NH}_4\text{SCN}$  solution. Mix and dilute to 100 ml. with water. To prepare the standard, treat 5 ml. of iron-free  $\text{H}_2\text{SO}_4$  in the same manner as the sample, in a second Nessler tube. Then, while agitating with a glass plunger, add a standard iron solution until the color matches that of the sample tube. (If the iron standard contains 0.00005 g. of iron per milliliter, each milliliter of it will represent 0.001% iron in the final solution.)

*Remarks.*—Some workers prefer to add initially 10.00 ml. of  $\text{H}_2\text{SO}_4$  to 30 ml. of water in a 150-ml. beaker. Then 10 ml. of concentrated  $\text{HCl}$  are added, and the solution is boiled for 3 min. to ensure complete solution of any iron-containing dust. After cooling, the solution is diluted exactly to 250 ml. Aliquots of this solution are then taken for the visual comparison procedure. The addition of  $\text{HCl}$  alters the color of the complex formed from red-brown to red, which may be easier to match.

*Photometric Procedure.*—Transfer an appropriate  $\text{H}_2\text{SO}_4$  sample (2 to 5 ml. of 93%+ or equivalent weight) to a 100-ml. volumetric flask containing about 50 ml. of water; cool to room temperature, add 0.1 *N*  $\text{KMnO}_4$  dropwise to the appearance of a faint pink color, and 20 ml. of an aqueous  $\text{NH}_4\text{SCN}$  solution (149 g. per liter), and dilute to mark with water. Prepare a reagent blank making the same addition of reagents but substituting iron-free  $\text{H}_2\text{SO}_4$ . Within 5 min. of the final mixing, measure the absorbance of the sample against the reagent blank, preferably with the use of a blue filter (425  $m\mu$ ), or with a green filter (525  $m\mu$ ). Read the result from a standard curve obtained by the use of standard solutions prepared in the manner of the sample but substituting iron-free sulfuric acid of similar concentration, and adding 0.0, 1.0, 3.0, 5.0, and 10.0 ml. of a standard  $\text{Fe}_2(\text{SO}_4)_3$  solution (1 ml. = 0.000025 g. of iron).

*Remarks.*—The absorbance deviates from Beer's law, and hence, the standard solutions should closely simulate the sample preparation, especially in the  $\text{NH}_4\text{SCN}$  concentration, and approximately in  $\text{H}_2\text{SO}_4$  content. If organic matter is present in the sample that is not decolorized by the gentle  $\text{KMnO}_4$  treatment, treat the sample successively with the following reagents, and fume or evaporate between

each addition:  $\text{HNO}_3$ ;  $\text{HNO}_3\text{-KClO}_3$ ; water; 1:1  $\text{HCl}$ ; and 1:1  $\text{H}_2\text{SO}_4$ . Heat the final  $\text{H}_2\text{SO}_4$  solution to expel  $\text{HCl}$ , cool, and employ it in the procedure. For extremely small amounts of iron, a spectrophotometric procedure should be substituted with the absorbance measured at about 485  $\text{m}\mu$ ; however, a 1,10-phenanthroline procedure may be preferred, as Beer's law is followed more closely. (See Vol. I, p. 553.)

Some workers prefer thiocyanate procedures for routine use, employing  $\text{KSCN}$  rather than  $\text{NH}_4\text{SCN}$ , and sometimes secure increased sensitivity by the addition of an organic solvent. (See Vol. I, pp. 552-3.)<sup>20a</sup>

As dust (especially fly ash) contains substantial amounts of iron, it is imperative that all glassware be carefully cleaned and protected from dust, and that the original plant sampling of the acid be conducted under dust-free conditions; otherwise, the analytical result may not be representative of the manufactured acid.

### DETERMINATION OF ZINC IN SULFURIC ACID

Large amounts of zinc in sulfuric acid may be determined gravimetrically as zinc oxide. Additional approaches include a precipitation titration with ferrocyanide (see Vol. I, pp. 1233-1239) and a chelometric titration with EDTA.<sup>21</sup> Small amounts of zinc are determined turbidimetrically as zinc ferrocyanide.

**Gravimetric Determination of Large Amounts of Zinc in Sulfuric Acid.**—Large amounts of zinc may be determined by the acid sulfide separation of copper, lead, etc., followed by precipitation of zinc sulfide from ammoniacal medium, ignition of the washed precipitate, then weighing as zinc oxide.

**Procedure.**—In a platinum or silica dish, fume 200 g. of the  $\text{H}_2\text{SO}_4$  sample (or other appropriate weight) to a volume of 2 to 5 ml. Add some water, neutralized with aqueous  $\text{NH}_3$ , and add sufficient dilute  $\text{H}_2\text{SO}_4$  to make 0.2 to 0.5  $N$  in free acid. Pass gaseous  $\text{H}_2\text{S}$ , and separate the sulfide precipitate by filtration (test for complete precipitation in the filtrate). Separate iron from the filtrate as iron(III) oxide by oxidation with bromine and addition of  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$ . Precipitate  $\text{ZnS}$  from the resulting filtrate made acid with formic acid by the passage of  $\text{H}_2\text{S}$ . Separate the precipitate in a tared Gooch crucible, wash, ignite to  $\text{ZnO}$ , and weigh. Express the increase in weight as percentage of  $\text{Zn}$  in the original sample.

**Remarks.**—For additional information on this method see Vol. I, p. 1231. The heavy metal separation can probably be made "cleaner" by the use of thioacetamide.<sup>22</sup>

**Turbidimetric Ferrocyanide Determination of Traces of Zinc in Sulfuric Acid.**—The usual procedure involves a visual comparison of the turbidity developed with ferrocyanide.

**Procedure.**—In a silica dish, evaporate an appropriate  $\text{H}_2\text{SO}_4$  sample (25 to 50 ml.) to dryness. Treat the residue with concentrated aqueous ammonia and  $\text{NH}_4\text{Cl}$  solution. Filter off the iron(III) hydroxide precipitated. Neutralize the

<sup>20a</sup> Also see Sandell, E. B., *Colorimetric Determination of Traces of Metals*, 3rd Ed., Interscience Publishers, Inc., New York, 1959, 524-37.

<sup>21</sup> The rapid determination of zinc in viscose spinning liquors containing  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  is of importance in the control of rayon production. An EDTA titration is appropriate. See Saito, M., Nagamura, S., and Ueno, K., *Chemist-Analyst*, 47, 67, 1958.

<sup>22</sup> Flaschka, H., and Jakoblevich, A., *Anal. Chim. Acta*, 4, 247, 1950; see also Swift, E. H., and Anson, F. C., in *Advances in Analytical Chemistry and Instrumentation*, C. N. Reilly, ed., Vol. 1, Interscience Publishers, Inc., New York, 1960, 293-345.

filtrate with 96% zinc-free  $\text{H}_2\text{SO}_4$  and add 10 ml. in excess. Now add a potassium ferrocyanide solution so that the solution is about 2.5% in this salt. Compare the turbidity developed with that of standards. (See also Vol. I, p. 1240.)

### DETERMINATION OF COPPER IN SULFURIC ACID

Copper in small amounts in sulfuric acid is determined colorimetrically. For routine control, the color of the copper(II)-ammine complex (or of a copper-ammine complex) may be evaluated either by a visual comparison procedure or by the use of a filter photometer. Where greater sensitivity is required, such chromogenic agents as diethyldithiocarbamate and 2,9-dimethyl-1,10-phenanthroline (Neocuproine) are applicable.<sup>23</sup>

**Visual Comparison and Photometric Procedure.**—Evaporate an appropriate amount of the  $\text{H}_2\text{SO}_4$  sample (25 to 50 ml.) to dryness. Take up the residue in 100 ml. of water and add 2 ml. of copper-free (reagent grade) HCl. Precipitate the copper by passage of  $\text{H}_2\text{S}$  gas or boiling with thioacetamide. Dissolve the washed precipitate in  $\text{HNO}_3$  and make the solution ammoniacal with concentrated aqueous ammonia. Match the blue color developed against that of similarly prepared standards containing known amounts of copper. Alternatively, employ a filter photometer and a filter transmitting in the region of 620  $\text{m}\mu$ .

**Remarks.**—A polyamine may be substituted to advantage. Triethylenetetramine (i.e., trien) and tetraethylenepentamine (i.e., tetren) are appropriate, using a filter transmitting in the region of 625 to 650  $\text{m}\mu$ ; nickel and cobalt do not interfere because of the improved sensitivity.<sup>24</sup> (See also Vol. I, p. 408.)

### DETERMINATION OF NICKEL IN SULFURIC ACID

In the application of purity grades of sulfuric acid (and of certain other mineral acids) in the electronics industry, contemporary interest exists in the trace nickel content. This may be estimated by spectrographic analysis (see page 552) or by a sensitive spectrophotometric method following an evaporation of a large sample (with sulfuric acid added in the case of other mineral acids). Some workers favor a dimethylglyoxime procedure with a chloroform extraction step in which iron(III) is masked by citrate and a subsequent oxidation (see Vol. I, pages 64, 178, 420, and 613). An  $\alpha$ -furildioxime procedure also offers good sensitivity and selectivity (with iron masked by citrate in the chloroform or *o*-dichlorobenzene extraction step) without an oxidation step.<sup>25</sup>

### DETERMINATION OF THE WATER CONTENT OF SULFURIC ACID

Where of interest, the water content of sulfuric acid (as well as of nitric, hydrofluoric, and hydrochloric acids) may be determined by a Karl Fischer titration, usually after neutralization of the acid with pyridine.<sup>26</sup>

<sup>23</sup> Sandell, E. B., *Colorimetric Determination of Traces of Metals*, Interscience Publishers, Inc., New York, 3rd Ed., 1959, 442–453; see also Vol. I, 407–410.

<sup>24</sup> Crumpler, T. B., *Anal. Chem.*, **19**, 325, 1947; Williams, L. H., *Analyst*, **75**, 425, 1950.

<sup>25</sup> Taylor, C. G., *Analyst*, **81**, 369, 1956; Gahler, A. R., Mitchell, A. M., and Mellon, M. G., *Anal. Chem.*, **23**, 500, 1951.

<sup>26</sup> See Mitchell, J., Jr., and Smith, D. M., *Aquametry*, Interscience Publishers, Inc., New York, 1948.



SPECTROGRAPHIC DETERMINATION OF IMPURITIES  
IN SULFURIC ACID

With the increased interest in mineral acids of high purity for use in the electronics and nuclear industries, the determination of elements present in trace amounts has received attention. Spectrographic methods are applicable and afford the advantage of simultaneously recording many impurities. By a preliminary concentration, determinations of impurities even at the level of 0.1 p. p. m. or less may be accomplished. Sulfuric acid may be analyzed spectrographically for Al, Fe, Cu, Sb, Pb, Ni, Ag, Au, Mn, Mg, Ca, Si, and Sn by the following procedure.

**Spectrographic Procedure.**—By weight or volume take a 100-g. sample of  $\text{H}_2\text{SO}_4$ . Place it in a platinum dish, add 0.5 ml. of  $\text{HNO}_3$  and evaporate in a dust-free atmosphere to a volume of about 10 ml. Add 100 mg. of spectrographic grade graphite powder as a collector, and evaporate to dryness. Weigh a 10-mg. portion of this residue and transfer it to a preformed  $\frac{1}{4}$ -in. graphite electrode, having a  $\frac{1}{8}$  by  $\frac{3}{16}$ -in. crater. Excite the sample in a direct current arc under appropriate conditions, e.g., 10 amp. for 90 sec. Excite commercial spectrographic standards prepared in graphite (0.1 to 0.0001% in the element) under the same conditions. All plates should be developed under identical conditions and the line densities compared (in the calculations, take account of the thousandfold concentration of the sample). The sample size may be adjusted depending upon the degree of concentration required for the detection and determination of the element of interest; the use of composite samples often leads to more representative results.

## ANALYSIS OF REAGENT GRADE SULFURIC ACID

For information on the specifications and recommended procedures for the analysis of reagent grade sulfuric acid, relevant monographs should be consulted.<sup>27</sup>

## OLEUM AND "MIXED ACID"

The terms oleum and fuming sulfuric acid are given to (concentrated) sulfuric acid containing "free" sulfur trioxide. Oleum is offered in various strengths ranging from 10 to 70% free  $\text{SO}_3$  (also termed % oleum). Common strengths offered in tonnage quantity include 20, 40 and 65% oleum (i.e., 104.5, 109.0, and 114.6%  $\text{H}_2\text{SO}_4$ ). Nitric acid is added, on request, by some producers to oleum (usually that of 40% free  $\text{SO}_3$ ) often to the extent of 3 to 6% to prevent freezing in winter months. Reagent grade fuming sulfuric acid, meeting American Chemical Society specifications, is available in three strengths, namely, 15–18, 20–23, and 30–35% free  $\text{SO}_3$ . Sulfur trioxide (99%  $\text{SO}_3$  minimum) is available in a stabilized form. "Mixed acid" or "nitrating acid" are common designations for mixtures of concentrated sulfuric acid or oleum with nitric acid and the common commercial strengths, expressed as %  $\text{HNO}_3$  and %  $\text{H}_2\text{SO}_4$ , include the following: 85, 12; 80, 15; 60, 38; 45, 53.

The conventional chemical analysis of the composition of oleum and mixed acid

<sup>27</sup> American Chemical Society, Reagent Chemicals—1960, Washington, D. C., 1961; Rosin, J., Reagent Chemicals and Standards, D. Van Nostrand Co., Inc., Princeton, New Jersey, 4th Ed., 1961; British Drug Houses Ltd. and Hopkin & Williams Ltd., Anal. Standards for Laboratory Chemicals, London, 5th Ed., 1957; Chemapol, Czechoslovak Fine Chemicals Standards, 2nd Ed., Vol. I, Prague, 1960; Japanese Industrial Standards Handbook, Reagent Chemicals, Nippon Kikaku Kyokai, Tokyo, 1961.

is based on the determination of the total acidity expressed as %  $\text{H}_2\text{SO}_4$  and the determination of total sulfuric acid content after volatilization of nitric acid. Both determinations are based on alkalimetric titrations (with a temperature rise method as an alternative for simple oleums). For oleum, a correction is applied for the sulfur dioxide content after its separate determination. The free sulfur trioxide content and total nitric acid (or  $\text{N}_2\text{O}_5$ ) content may be then established from these results by stoichiometry or may be separately determined. Variations and alternatives to this approach are noted as remarks to the following procedures.

### TOTAL ACIDITY OF OLEUM OR MIXED ACID (TITRATION METHOD)

*Procedure.*—By use of a Dely tube or weighing buret, with the techniques given on pages 535–9, add a weighed sample of oleum or mixed acid (sufficient to neutralize 80–95 ml. of 1 *N* NaOH, that is, equivalent to 3.9–4.7 g. of 100%  $\text{H}_2\text{SO}_4$ ) to 150 ml. of cold water in a glass-stoppered conical flask or bottle. Seat the stopper and agitate the contents. Allow the solution to cool. Titrate the total acidity with 1 *N* NaOH in the manner described for  $\text{H}_2\text{SO}_4$  (page 540). The % Total Acidity as  $\text{H}_2\text{SO}_4$  = (ml. of NaOH, corrected for temperature)  $\times$  (normality of NaOH)  $\times 0.049039 \times 100 \div$  (sample weight in g.). The % Free  $\text{SO}_3$  (uncorrected) =  $4.4441 \times (\% \text{ Total Acidity as } \text{H}_2\text{SO}_4 - 100.0)$ .

*Remarks.*—The result must be corrected for other acids present to obtain the “true”  $\text{H}_2\text{SO}_4$  content or “true” free  $\text{SO}_3$  content. (See further under the calculation of the composition of oleum and mixed acid.) With mixed acid and oleum of large free  $\text{SO}_3$  content, the sample is expediently weighed in a sealed ampoule or bulb (see page 538 for this technique). The bulb is broken, best by violent shaking, under the surface of the major portion of the NaOH with added water required in the titration placed in a glass-stoppered flask or bottle.

For rapid, routine analysis, it is expedient to drown a large sample of the oleum or mixed acid by the following technique: A 6-in. glass funnel is suspended from a ring stand over a 1000-ml. volumetric flask and its tube is extended by a short section of rubber tubing and glass tubing so that it reaches to the bottom of the flask. The funnel outlet is closed by a clamp in the rubber connection (or alternatively by a small stopper fastened to a small glass rod positioned in the apex of the funnel). The funnel is filled with water and about 50 ml. of water run into the flask by opening the closure briefly. The acid sample is pipetted into a tared weighing bottle and weighed. The bottle is then inverted under the water in the funnel and the bottle stopper removed slowly by glass-tipped forceps. When all the acid has poured out, the stopper is removed and left in the water and the bottle is sloshed until all fumes are absorbed. It is then allowed to fill with water. The bottle and its stopper (and the tongs) are then removed from the funnel with water rinses. The contents of the funnel are allowed to drain into the flask followed by water rinses. The solution is diluted to mark with water and mixed. Portions (100 ml.) of this solution are then employed in the titration of the total acidity and of the total sulfuric acid content. Portions may also be used for the determination of various impurities in the original sample, where this information is of interest to the analyst.

TOTAL ACIDITY OF OLEUM (TEMPERATURE RISE METHOD)<sup>28</sup>

**Procedure.**—Measure *A* ml. of standard *B* into a graduated cylinder of capacity *C* ml. (dry or wet with the standard) as follows:

Sample, % $\text{H}_2\text{SO}_4$	Standard ( <i>B</i> ) nature, % $\text{H}_2\text{SO}_4$	Ml. of standard taken ( <i>A</i> )	Capacity of cylinder, ml. ( <i>C</i> )
95.5–100.0	104.5–105	50	50
100.4–106.0	93.19 (66° Be)	50	50
> 105.0	93.19 (66° Be)	150	250

Transfer to the Dewar flask (silvered, pear-shaped, 250-ml. capacity, mounted in wooden box with mineral wool packing and with the neck protruding about 0.5 inch through a sheet lead cover to the box). Insert the thermometer ( $-5^\circ$  to  $220^\circ\text{F}$ ,  $1^\circ$  divisions, calibrated) and record the temperature as  $T_1$ . Measure 50 ml. of the sample into a separate 50-ml. graduated cylinder (which has been first rinsed with the sample); with the same thermometer (washed with water and wiped dry), measure and record the temperature as  $T_2$ . Read the temperature in both cases with the mercury column immersed in the liquid since the heat of reaction of the acid with atmospheric moisture may give a false value. The temperatures  $T_1$  and  $T_2$  should be in the range  $75$ – $90^\circ\text{F}$ . (or  $80$ – $90^\circ\text{F}$ . for  $> 105\%$   $\text{H}_2\text{SO}_4$ ). Transfer the thermometer to the Dewar flask and pour the sample into this flask. With the thermometer bulb immersed in the mixture and touching the flask bottom, mix the contents by gentle shaking and swirling for 60 seconds. Record the observed temperature as  $T_f$ .

**Calculations and Remarks.**—The method is not applicable to oleums containing nitric acid and is unreliable for total acidities between 100.0 and 100.4%  $\text{H}_2\text{SO}_4$  (and a titration should be here applied). The temperature rise  $R$  is obtained from the experimental temperatures from the equation  $R = T_f - \frac{1}{2}(T_1 + T_2)$ , where equal volumes of the sample and standard are taken; for  $> 105.0\%$   $\text{H}_2\text{SO}_4$ , the equation takes the form  $R = T_f - \frac{1}{4}(3T_1 + T_2)$ . The % Total Acidity is then calculated from tables or graphical plots based on samples and standards of known composition as established by precision alkalimetric titrations. Standards should be checked from time to time against the established tables or plots. The calibration strictly applies to a given Dewar flask; however, it may prove to be sufficiently exact for Dewar flasks of the same manufacturer, especially if selection is based on actual performance or by comparison of the heat transfer properties by placement of a standard heat source in the various flasks. For the indicated size Dewar flask and the above procedure, the calibration for the 95.5–100.0%  $\text{H}_2\text{SO}_4$  range should possibly cover the temperature rise in  $^\circ\text{F}$ . of  $0$ – $53^\circ$ ; for 100.4–106.0%  $\text{H}_2\text{SO}_4$ ,  $8$ – $76^\circ$ ; for  $> 105\%$   $\text{H}_2\text{SO}_4$ ,  $37$ – $136^\circ\text{F}$ . The % Total Acidity can, of course, be expressed as %  $\text{SO}_3$ .

Diverse methods have been reported for the determination of the free sulfur trioxide content or total acidity of oleum including titrations with water to thermo-

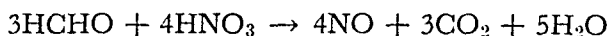
<sup>28</sup> Procedure, courtesy, E. I. DuPont de Nemours & Co., Inc., based on Howard, H., J. Soc. Chem. Ind., 29, 3, 1910, and Curtis, R., and Miles, F., *ibid.*, 39, 64, 1920.

metric or potentiometric end points, precision calorimetry on the addition of water, and various physical measurements including density and viscosity. However, such methods appear not to have received widespread, routine application.<sup>29</sup> Measurement of the specific conductivity is suitable for at least 18–23% oleum, but close control of the temperature is imperative and variations in impurity may be a serious source of error.<sup>29</sup> Conductometry has also been proposed with close thermostatic control of temperature for the establishment of the composition of mixed acids in terms of sulfuric acid, nitric acid, and water; however, the results are about 5% lower for the water content than the value derived by the conventional chemical analysis.<sup>30</sup>

### TOTAL SULFURIC ACID IN OLEUM OR MIXED ACID

**Procedure.**—By the use of the Dely tube or other suitable technique (see pages 535 through 539) establish a sample of the oleum or acid requiring 80–85 ml. of 1 N NaOH in the titration of total  $\text{H}_2\text{SO}_4$  and run under 45–50 ml. of *cold* water. Evaporate the solution on a steam bath, thus expelling volatile acids, oxides of nitrogen, and nitric acid, with the aid of a gentle stream of filtered, preferably warm air, to the first signs of darkening (due to charring of organic matter present in the sample or dust particles from the air). Check for the removal of nitric acid by removing the dish from the bath and sniffing the air over the dish. If acid is noted, continue the evaporation further.<sup>31</sup> Rinse down the walls of the dish with 5 ml. of water and evaporate as before. Titrate the total sulfuric acid with 1 N NaOH in the manner described for sulfuric acid (page 540). The % Total  $\text{H}_2\text{SO}_4$  = (ml. of NaOH, corrected for temperature)  $\times$  (normality of NaOH)  $\times$   $0.049039 \times 100 \div$  (weight of sample in grams).

**Remarks.**—Since the evaporation in the above procedure is tedious, the determination of total sulfuric acid should be started as the first step in the conventional analysis of an oleum or a mixed acid. The reproducible, yet complete volatilization of nitric acid without loss of sulfuric acid in the evaporation of mixed acids has often been questioned. In one study the loss of sulfuric acid was found to vary from nil to 0.02% total  $\text{H}_2\text{SO}_4$ .<sup>32</sup> As an alternative to evaporation of nitric acid, its destruction with formaldehyde has been proposed:



Any formic acid also formed is volatilized as its methyl ester by the addition of methanol. The sulfate is then titrated in hot solution with barium acetate to a conductometric end point with a claimed reliability of 0.1%  $\text{H}_2\text{SO}_4$ . The presence of propanol increases the sharpness of the end point.<sup>33</sup>

<sup>29</sup> For summary of literature, see M. R. Singer, in *The Manufacture of Sulfuric Acid*, Duecker, W. W., and West, J. R., Reinhold Publishing Corp., New York, 1959, pages 423–426; for the conductivity method, circuitry and a cell design are presented.

<sup>30</sup> Lacroix, Y., and Chaverou, M., *Mém. Poudres*, 41, 423, 1959; through *Anal. Abstracts*, 7, 5222, 1960.

<sup>31</sup> The full removal of nitric acid may then be followed by noting whether moistened blue litmus paper held over the dish is turned red. A further simple test involves placement of a strip of ordinary paper towelling in the vapors; development of a brown color is indicative of nitric acid or oxides of nitrogen (see A. Chan, Jr., *J. Chem. Educ.*, 38, 412, 1961).

<sup>32</sup> Unpublished work, staff, E. I. DuPont de Nemours & Co., Inc.

<sup>33</sup> Clark, J. D., in *Analytical Procedures for Rocket Propellants*, VII, Mixed Acid, Report No. 24, U. S. Naval Air Rocket Test Station, Lake Denmark, N. J., 1952; C. A., 48, 3692, 1955.

## ACTUAL NITRIC ACID IN MIXED ACID

**Procedure.**—Although  $\text{HNO}_3$  may be calculated from the stoichiometry of the mixed acid (or oleum) sample (see below), the direct determination is often desirable and affords greater accuracy. The titrimetric iron(II) sulfate procedure given for nitric acid in sulfuric acid is applicable with the special remarks presented concerning the use of the method with mixed acids (see page 543). It should be observed that by this method the *actual* nitric acid content is obtained. If the *total* nitric acid content is sought (as is secured in essence by a nitrometer procedure), the nitrososulfuric acid content should be separately determined (e.g., by the permanganate titration procedure considered below) and be added to the actual nitric acid content. Often, however, the nitrososulfuric content may be small enough to allow its neglect.

## TOTAL NITRIC ACID IN MIXED ACID

**Nitrometer Procedure.**—See Vol. I, pages 758–759 for the full operational details. As noted above, the result corresponds to *total* nitrogen compounds expressed as nitric acid and thus includes any nitrososulfuric acid present in the sample.

**Calculation of Total Nitric Acid in Mixed Acid.**—The total nitric acid content may be calculated for a mixed acid from the results of the determination of total acidity and the total sulfuric acid determination since sulfurous acid (sulfur dioxide) cannot exist in a mixed acid: The % Total  $\text{HNO}_3$  = (% Total Acidity as  $\text{H}_2\text{SO}_4$  - % Total  $\text{H}_2\text{SO}_4$ )  $\times$  1.2850. The fact that the difference between two experimentally derived values is involved seriously impairs the reliability of the calculation when only a small amount of nitric acid is present.

## NITROSOSULFURIC ACID IN MIXED ACID

**Procedure.**—Transfer a suitable sample to 150 ml. of water and titrate promptly with (freshly standardized) 0.1 *N* ( $\approx$  0.02 *M*)  $\text{KMnO}_4$ , to an end point marked by the persistence of a pink color for at least 60 seconds after the addition of a single drop. %  $\text{NOHSO}_4$  = (ml. of  $\text{KMnO}_4$ )  $\times$  (normality of  $\text{KMnO}_4$ )  $\times$  0.06354  $\times$  100  $\div$  (sample weight in grams).

The solution should not be stirred more than necessary until the end point is approached. Back-titration procedures and cerate titrations are also feasible (see Remarks under determination of nitrous acid in nitric acid, page 562). In the interested industries, the term "nitrososulfuric acid" (or its equivalent "nitrosylsulfuric acid") has long usage. Modern evidence suggests that the moiety involved is ionized in absolute  $\text{H}_2\text{SO}_4$  and is the salt, nitroso hydrogen sulfate,  $\text{NO}^+$ ,  $\text{HSO}_4^-$ ; this finding does not invalidate the conventional calculations since the acid sulfate ion is a monoprotic acid. In water, the moiety passes to a mixture of nitrous and sulfuric acids.

CALCULATION OF RESULTS FOR OLEUM FREE OF  $\text{SO}_2$ 

For an oleum free of  $\text{SO}_2$  (and of  $\text{HNO}_3$ ), the calculation is relatively simple. Either the % Total Acidity as  $\text{H}_2\text{SO}_4$  or the % Free  $\text{SO}_3$  has been determined and may be interconverted by use of the Table on page 616 or by the following equations.

NOTE. These equations are derived by writing the expressions for % Total  $\text{SO}_3$ , % Combined  $\text{H}_2\text{O}$ , % Combined  $\text{SO}_3$ , and % Free  $\text{SO}_3$  and intersubstituting. Analogous equa-

tions may be derived for oleum containing  $\text{SO}_2$  (or mixed acid). For example for oleum containing  $\text{SO}_2$ :  $\% \text{ Free SO}_2 = 4.4441 \times (\% \text{ Total Acidity as H}_2\text{SO}_4 - 100.00) - 2.360 \times \% \text{ SO}_2$ . However, the stepwise calculations given for oleum containing  $\text{SO}_2$  and mixed acid are preferred by most workers.

$$\% \text{ Total Acidity as H}_2\text{SO}_4 = 0.22502 \times \% \text{ Free SO}_3 + 100.00$$

$$\% \text{ Free SO}_3 = 4.4441 \times (\% \text{ Total Acidity as H}_2\text{SO}_4 - 100.00)$$

Alternatively the Actual  $\% \text{ H}_2\text{SO}_4$  may be calculated and reported with the  $\% \text{ Free SO}_3$ ; the two obviously must add to 100%.

$$\% \text{ Actual H}_2\text{SO}_4 = 5.4441 (100.00 - 0.81632 \times \% \text{ Total Acidity as H}_2\text{SO}_4)$$

or

$$\% \text{ Actual H}_2\text{SO}_4 = 100.00 - \% \text{ Free SO}_3$$

*Example.*—An oleum is found to contain 102.2% Total Acidity as  $\text{H}_2\text{SO}_4$ . Then  $\% \text{ Free SO}_3 = 4.4441 (102.2 - 100.0) = 9.8\%$  and  $\% \text{ Actual H}_2\text{SO}_4 = 90.2\%$ .

#### CALCULATION OF RESULTS FOR OLEUM CONTAINING $\text{SO}_2$

If a significant amount of  $\text{SO}_2$  is present in an oleum and is determined (see below), the following relationships apply:

$$\% \text{ Total H}_2\text{SO}_4 = \% \text{ Total Acidity as H}_2\text{SO}_4 - 1.531 \times \% \text{ SO}_2^{33a}$$

$$\% \text{ Total SO}_3 = \% \text{ Total H}_2\text{SO}_4 \times 0.81631$$

$$\% \text{ Combined H}_2\text{O} = 100.00 - (\% \text{ Total SO}_3 + \% \text{ SO}_2)$$

$$\% \text{ Combined SO}_3 = \% \text{ Combined H}_2\text{O} \times 4.4441$$

$$\% \text{ Free SO}_3 = \% \text{ Total SO}_3 - \% \text{ Combined SO}_3$$

$$\% \text{ Actual H}_2\text{SO}_4 = \% \text{ Combined SO}_3 + \% \text{ Combined H}_2\text{O}$$

*Example.*—What is the composition of an oleum found to contain 2.00%  $\text{SO}_2$  and 102.29% Total Acidity as  $\text{H}_2\text{SO}_4$ ?

$$\% \text{ Total H}_2\text{SO}_4 = 102.29 - 1.531 \times 2.00 = 99.23\%$$

$$\% \text{ Total SO}_3 = 99.23 \times 0.81631 = 81.00\%$$

$$\% \text{ Combined H}_2\text{O} = 100.00 - (81.00 + 2.00) = 17.00\%$$

$$\% \text{ Combined SO}_3 = 17.00 \times 4.4441 = 75.55\%$$

$$\% \text{ Free SO}_3 = 81.00 - 75.55 = 5.45\%$$

$$\% \text{ Actual H}_2\text{SO}_4 = 75.55 + 17.00 = 92.55\%$$

Report:  $\text{H}_2\text{SO}_4$ , 92.55%;  $\text{SO}_3$ , 5.45%;  $\text{SO}_2$ , 2.00%; total, 100.00%.

<sup>33a</sup> The factor 1.531 assumes that phenolphthalein is used in the titration of the total acidity; if methyl orange is used, the factor should be 3.062.

## CALCULATION OF RESULTS FOR MIXED ACID

Where the % Total Acidity as  $\text{H}_2\text{SO}_4$  and % Total  $\text{H}_2\text{SO}_4$  have been determined the % Total  $\text{HNO}_3$  may be calculated as given on page 556:

$$\% \text{ Total HNO}_3 = (\% \text{ Total Acidity as H}_2\text{SO}_4 - \% \text{ Total H}_2\text{SO}_4) \times 1.2850$$

Alternatively the total  $\text{HNO}_3$  content may be determined (see above). If the nitrososulfuric acid content is determined:

$$\% \text{ Actual H}_2\text{SO}_4 = \% \text{ Total H}_2\text{SO}_4 - (\% \text{ NOHSO}_4 \times 0.7718)$$

$$\% \text{ Actual HNO}_3 = \% \text{ Total HNO}_3 - (\% \text{ NOHSO}_4 \times 0.4960)$$

Alternatively the actual  $\text{HNO}_3$  content is determined (see above).

The water content of the mixed acid can then be estimated:

$$\% \text{ H}_2\text{O} = 100.00 - (\% \text{ NOHSO}_4 + \% \text{ Actual H}_2\text{SO}_4 + \% \text{ Actual HNO}_3)$$

If the %  $\text{H}_2\text{O}$  is negative, it may be expressed as "minus" water, the physical meaning of which is that free  $\text{SO}_3$  is present, that is, an excess of oleum is present in the mixed acid.

Where an excess of oleum is present (free  $\text{SO}_3$  present), the calculation may take the following course, in which nitric acid is considered as present as its anhydride,  $\text{N}_2\text{O}_5$ .

$$\% \text{ Total N}_2\text{O}_5 = (\% \text{ Total Acidity as H}_2\text{SO}_4 - \% \text{ Total H}_2\text{SO}_4) \times 1.1013$$

$$\% \text{ Total SO}_3 = \% \text{ Total H}_2\text{SO}_4 \times 0.81631$$

$$\% \text{ Combined H}_2\text{O} = 100.00 - (\% \text{ Total SO}_3 + \% \text{ Total N}_2\text{O}_5)$$

$$\% \text{ Combined SO}_3 = \% \text{ Combined H}_2\text{O} \times 4.4441$$

$$\% \text{ Free SO}_3 = \% \text{ Total SO}_3 - \% \text{ Combined SO}_3$$

$$\% \text{ Actual H}_2\text{SO}_4 = \% \text{ Combined SO}_3 + \% \text{ Combined H}_2\text{O}$$

*Example.*—What is the composition of a mixed acid, if the Total Acidity as  $\text{H}_2\text{SO}_4$  was found to be 102.90% and the Total  $\text{H}_2\text{SO}_4$  100.45% (the %  $\text{N}_2\text{O}_5$  or %  $\text{HNO}_3$  was not determined)?

$$\% \text{ N}_2\text{O}_5 = (102.90 - 100.45) \times 1.1013 = 2.70\%$$

$$\% \text{ Total SO}_3 = 100.45 \times 0.81631 = 82.00\%$$

$$\% \text{ Combined H}_2\text{O} = 100.00 - (82.00 + 2.70) = 15.30\%$$

$$\% \text{ Combined SO}_3 = 15.30 \times 4.4441 = 67.99\%$$

$$\% \text{ Free SO}_3 = 82.00 - 67.99 = 14.01\%$$

$$\% \text{ Actual H}_2\text{SO}_4 = 67.99 + 15.30 = 83.29\%$$

Report:  $\text{H}_2\text{SO}_4$ , 83.29%;  $\text{SO}_3$ , 14.01%;  $\text{N}_2\text{O}_5$ , 2.70%; total, 100.00%.

DETERMINATION OF SULFUROUS ACID (SULFUR DIOXIDE)  
IN OLEUM

The determination of sulfurous acid in oleum parallels the iodimetric procedure given for sulfuric acid (see page 545). Sulfur dioxide cannot exist in an oleum with nitric acid, that is, in a mixed acid.

## DETERMINATION OF OTHER IMPURITIES IN OLEUM

Impurities in oleum and mixed acid are determined by the procedures given for sulfuric acid (pages 546–52) and where necessary or appropriate after an initial evaporation to remove free sulfur trioxide and nitric acid. This includes residue on ignition and lead. Less frequent determinations include iron, and arsenic. For arsenic in oleum and mixed acid a sample containing 1 to 20 micrograms of arsenic as  $\text{As}_2\text{O}_3$  (usually about 3 ml.) is placed in a dry 100-ml. beaker (and with oleum a few crystals of potassium nitrate are added). The beaker is covered with a watch glass and heated over a small flame until all free  $\text{SO}_3$  is removed (i.e., until bubbles become few and the atmosphere in the beaker suddenly becomes cloudy and then clears). To the cooled solution, 5 ml. of water is added cautiously and the resulting solution is taken almost to fumes on a hot plate and allowed to cool. The general Gutzeit procedure may then be applied as given in Vol. I, pages 118–124 (see also the remarks on page 546).

See the relevant monographs in footnote 27 for the analysis of reagent grade fuming sulfuric acid.

## NITRIC ACID

Nitric acid,  $\text{HNO}_3$ , of contemporary manufacture is relatively pure, and is offered commercially in a variety of strengths from dilute solutions to fuming acid. The principal strengths offered in the United States include 36°, 38°, 40°, and 42° Baumé, Heavy (i.e., 52.3%, 56.5%, 61.4%, and 67.2%  $\text{HNO}_3$ ), and the nominal percentage strengths 90% (47.8° Baumé), 95% (48.50° Baumé), and 100%. "Constant" boiling nitric acid is about 68.0 to 68.5%  $\text{HNO}_3$ , and boils at about 251°F., 121.6°C. The term "fuming acid" is applied to any strength greater than 85.7%  $\text{HNO}_3$  containing oxides of nitrogen. Red fuming nitric acid contains large amounts of the oxides of nitrogen (5 to 20% expressed at  $\text{NO}_2$ ) and has a total acidity greater than 100%  $\text{HNO}_3$ . "White" fuming nitric acid ("WFN" or "WFNA," 97.5 to 99.8%  $\text{HNO}_3$  ca. 0.5%  $\text{NO}_2$ ) and red fuming nitric acid ("RFN" or "RFNA" often ca. 12%  $\text{NO}_2$  with 0.6% HF added as a corrosion inhibitor) receive attention as oxidizers in rocket propellant systems (see p. 562). Reagent grade nitric acid, meeting American Chemical Society specifications, is available as 69.0 to 71.0%  $\text{HNO}_3$  (sp. gr. 1.42), fuming acid (90%), and red fuming acid (ca. 20%  $\text{NO}_2$ ). Mixtures of nitric and sulfuric acid ("mixed acid," "nitrating acid") are considered with oleum (see p. 552). Acid etch mixtures containing nitric acid are briefly considered on p. 585.

## NITRIC ACID CONTENT

*Nitric Acid Content by Specific Gravity.*—The estimation of nitric acid content by the use of a hydrometer is feasible over the entire range of practical concentrations up to 100%  $\text{HNO}_3$ . Specific gravity-composition tables for nitric acid are given on pp. 617 through 620.



**Nitric Acid Content by Alkalimetric Titration.**—The procedure for the determination of the total acidity of nitric acid by acid-base titrimetry parallels that given for sulfuric acid (p. 540), and hence, requires only an abbreviated statement here:

**Procedure.**—Place 100 to 150 ml. of  $\text{CO}_2$ -free water in a 110-mm. casserole, add a nitric acid sample (equivalent to 2.5 to 3.0 g. of 100%  $\text{HNO}_3$ ), and titrate with 0.5 *N* NaOH to the phenolphthalein end point. Note the temperature of the NaOH solution and add a correction of 0.00030 ml. per milliliter of 0.5 *N* NaOH for each degree Centigrade below its standardization temperature; or subtract the correction for each degree above.

**Remarks.**—For fuming nitric acid, use of the special confined weighing techniques, such as the Dely tube (see p. 537), is mandatory, and absorption in an excess of 0.5 *N* NaOH, followed by back titration with standard  $\text{H}_2\text{SO}_4$  is expedient. The sample size given is appropriate for the 75-ml. bulb of a chamber buret (see footnote 3, p. 536). Some workers prefer the use of a 1 *N* NaOH; others of 0.333 . . . *N* NaOH. Other indicators may be employed including methyl red; this indicator will be bleached by any nitrous acid present, however, and addition of a further amount of indicator may be required as the end point is reached. A potentiometric end point is also feasible.

**Calculation.**

% Total Acidity as  $\text{HNO}_3$

$$= \frac{(\text{milliliters of NaOH}) \times (\text{normality of NaOH}) \times 0.063013 \times 100}{\text{sample weight in grams}},$$

where the volume of NaOH is corrected for temperature. If the sample contains significant amounts of other acids, a correction may be applied following their determination. For example, %  $\text{HNO}_3$  = % Total Acidity as  $\text{HNO}_3$  - (%  $\text{H}_2\text{SO}_4 \times 1.285$ ) - (%  $\text{HCl} \times 1.728$ ) - (%  $\text{HNO}_2 \times 1.340$ ).

## DETERMINATION OF SULFURIC ACID IN NITRIC ACID

Sulfuric acid, present in amounts greater than about 0.02%, is best determined, following the evaporation of nitric acid on a steam bath, either by an acid-base titration, or gravimetrically, as barium sulfate. Small contents of sulfuric acid are usually determined turbidimetrically either by a visual comparison or photometric procedure.

**Titrimetric Procedure for Sulfuric Acid.**—Weigh out about 2.0 g. of the  $\text{HNO}_3$  in a 250-ml. beaker on a platform balance to the nearest 0.1 g. Evaporate essentially to dryness on a steam bath, hastening the evaporation, if preferred, by directing a gentle stream of filtered air on the surface of the liquid. Dissolve the residue in 5 ml. of water, washing down the beaker walls well, and repeat the evaporation and re-solution steps until nitric acid fumes cease to be evolved. Cool and dilute to 100 ml. with  $\text{CO}_2$ -free water, and titrate with 0.05 *N* NaOH to a faint pink phenolphthalein end point. The %  $\text{H}_2\text{SO}_4$  = (milliliters of NaOH solution)  $\times$  (normality of NaOH)  $\times$  0.04904  $\times$  100  $\div$  (sample weight in grams).

**Gravimetric Procedure for Sulfuric Acid.**—This determines both sulfuric acid and sulfate "bound" with iron or other metals. To the residue from the first steam bath evaporation (see titrimetric procedure above), add 2 ml. of concentrated HCl. Dilute to about 100 ml. with water. Heat to boiling, and add 10 ml.

of  $\text{BaCl}_2$  solution (10%) dropwise. Complete the determination according to the conventional procedure (see Vol. I, pp. 1007–1008). The total sulfate as %  $\text{H}_2\text{SO}_4$  =  $(\text{BaSO}_4 \text{ weight in grams}) \times 0.4202 \times 100 \div (\text{sample weight in grams})$ .

**Visual Comparison Turbidimetric Procedure.**—Take a suitable sample of  $\text{HNO}_3$  containing 0.01 to 0.05 mg. of  $\text{H}_2\text{SO}_4$ . Add 10 mg. of  $\text{Na}_2\text{CO}_3$  and evaporate to dryness on a steam bath. Dissolve the residue in 5 ml. of water and filter through a small filter paper (freshly washed with water slightly acidified with hydrochloric acid), collecting the filtrate in a test tube. Wash the paper twice with 2-ml. portions of water and dilute the collected filtrate to 10 ml. Add 1 ml. of  $\text{HCl}$  (1:9) and 1 ml. of  $\text{BaCl}_2$  solution (10%), which should be freshly filtered in order to assure a suitable fine precipitate. Stir briefly and after 10 min., compare the turbidity with that developed by standards equivalent to 0.01 to 0.05 mg. of  $\text{H}_2\text{SO}_4$ . These standards are prepared by adding 1.0, 2.0, . . . , 5.0 ml. of a  $\text{Na}_2\text{SO}_4$  solution (0.0146 g. of reagent grade anhydrous  $\text{Na}_2\text{SO}_4$  dissolved and diluted with water to 1000 ml.; 1 ml. = 0.01 mg. of  $\text{H}_2\text{SO}_4$ ) to matched test tubes, and diluting to 10 ml. with water. The result may optionally be expressed as percentage of  $\text{SO}_4$ .

**Instrumental Photometric Procedure for Sulfuric Acid.**<sup>34</sup>—In a beaker by weight or volume, establish a  $\text{HNO}_3$  sample containing 0.2 to 1.2 mg. of  $\text{H}_2\text{SO}_4$  (but not more than 10 ml. of 70%  $\text{HNO}_3$ ). Add 1 ml. of  $\text{NaCl}$  solution (10 g.  $\text{NaCl}$  in 90 ml. of water) and 3 or 4 glass beads. Evaporate to dryness on a steam bath, cool, and rinse down the beaker walls with 10 ml. of  $\text{HCl}$  (1:10). Again evaporate to dryness. Dissolve the residue in  $60 \pm 1$  ml. of water and transfer to a 100-ml. beaker. (Do not rinse the first beaker.) To the solution add 1 ml. of  $\text{HCl}$  (1:10) and 1 ml. of gum arabic solution (0.5 g. of the gum in 100 ml. filtered through a cotton plug) and mix. Add 0.16 to 0.18 g. of screened reagent grade barium nitrate (pass through 30- and 40-mesh screens; use crystals retained on the 40-mesh screen) and stir continuously until the reagent has dissolved. Transfer the mixture to a cuvet and measure the absorbance versus water in a filter photometer, using a blue filter. With very small amounts of sulfuric acid, the development of turbidity may be slow to reach a maximum, but when reached, the absorbance is stable for possibly 30 min. Run a reagent blank versus water and subtract its absorbance. Read the result from a calibration curve prepared by carrying 2.0, 4.0, . . . , 12.0 ml. of a  $\text{Na}_2\text{SO}_4$  solution (0.1463 g. of anhydrous reagent grade  $\text{Na}_2\text{SO}_4$  dissolved and diluted with water exactly to 1000 ml.; hence, 1 ml. = 0.10 mg. of  $\text{H}_2\text{SO}_4$ ).

**Remarks.**—The turbidity produced depends on the particle size of barium nitrate used; hence, the screening of the salt. The result may, of course, be expressed as percentage of  $\text{SO}_4$  rather than as percentage of  $\text{H}_2\text{SO}_4$ .

Since following the evaporation of nitric acid, a relatively simple system is present, the determination of trace sulfate based on metathesis with barium chloranilate and photometric measurement of the acid chloranilate ion "freed" is also applicable.<sup>35</sup>

## DETERMINATION OF HYDROCHLORIC ACID IN NITRIC ACID

At the low concentration of hydrochloric acid encountered in contemporary commercial nitric acid, a turbidimetric method based on the precipitation of silver chloride may be recommended. The procedure is essentially that given for hydro-

<sup>34</sup> Procedure, courtesy General Chem. Div., Allied Chem. Corp.

<sup>35</sup> Bertolacini, R. J., Barney, J. E., II, *Anal. Chem.*, **29**, 281, 1957.

chloric acid in sulfuric acid (see p. 542); but in the preparation of standards, chloride-free nitric acid is substituted for the sulfuric acid. Some workers prefer to neutralize the diluted nitric acid sample with ammonia, and to make acid with a few drops of nitric acid prior to the addition of the silver nitrate solution. The standards must then be prepared by adding the same amount of ammonia and neutralizing with chloride-free nitric acid to the same final acidity. A nephelometric procedure may be substituted (see Vol. I, pp. 333-4); the addition of a nonionic surfactant (Tween 20) may be warranted in order to stabilize the preparation.<sup>35a</sup>

### DETERMINATION OF NITROUS ACID (LOWER OXIDES OR DISSOLVED OXIDES) IN NITRIC ACID

By a permanganate titration, nitrous acid and lower oxides of nitrogen ( $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$ , and  $\text{N}_2\text{O}_4$ ) may be readily determined in nitric acid. The result may be expressed in terms of any of these substances.

**Procedure.**—To 250 ml. of water in a casserole, add 0.1 *N* (i.e., 0.02 *M*)  $\text{KMnO}_4$  dropwise and with stirring, until a faint pink color persists. Then add the  $\text{HNO}_3$  sample (20 g. or a suitable amount to give a titration result of at least 1 ml. of 0.1 *N*  $\text{KMnO}_4$ ). Titrate promptly with 0.1 *N*  $\text{KMnO}_4$  to a pink color that persists for 3 min.

**Calculations.**

$$\% \text{HNO}_2 = \frac{(\text{milliliters of KMnO}_4) \times (\text{normality of KMnO}_4) \times 0.02351 \times 100}{\text{sample weight in grams}}$$

Where it is desired to express the result as oxides of nitrogen, use the same formula substituting the following factors: for percentage of  $\text{N}_2\text{O}_3$ , 0.01898; for percentage of  $\text{N}_2\text{O}_4$ , 0.04601.

**Remarks.**—Since the volatilization of the oxides of nitrogen is appreciable, the titration medium should not be stirred other than most gently until the end point is approached. Since the reaction with  $\text{KMnO}_4$  is slow the 3-min. time specified should not be shortened. Because of these limitations, addition of an excess of  $\text{KMnO}_4$  and back-titration with iron(II) or oxalate is often preferred (e.g., see Vol. I, p. 747). Where organic matter is present in the  $\text{HNO}_3$ , an iodimetric procedure is appropriate. Procedures involving back-titration of an excess of cerium(IV) ammonium sulfate with iron(II), or oxalate to the *o*-phenanthroline or nitrophenanthroline end point are also to be recommended.<sup>35b</sup>

### DETERMINATION OF HYDROFLUORIC ACID IN NITRIC ACID

Traces of fluoride in nitric acid may be determined by a Willard-Winter distillation from sulfuric acid after a 1:10 dilution of the (concentrated) nitric acid sample (see Vol. I, Chapter 18). A finish of choice would be the spectrophotometric method based on the formation of the cerium(III)-fluoride-[(3,4-dihydroxy-2-anthraquinonyl)methyl]iminodiacetate complex.<sup>36</sup>

Red fuming nitric acid containing about 12% nitrogen dioxide, used as a rocket fuel oxidizer, may have 0.6% hydrofluoric acid added as a corrosion inhibitor.

<sup>35a</sup> Blanc, P., Bertrand, P., Liandier, M., *Chim. anal.*, **38**, 156, 1956.

<sup>35b</sup> United Kingdom Atomic Energy Authority, P. G. Rept. 69(W), *Analytical Methods for the Inspection of Nitric Acid*, H. M. Stationary Office, London, 1960; U. S. Military Specification MIL-N-7254C, *Nitric Acid, Fuming Technical*, July 1956; Stubblefield, F. M., *Ind Eng. Chem., Anal. Ed.*, **16**, 366, 1944.

<sup>36</sup> Belcher, R., Leonard, M. A., West, T. S., *Talanta*, **2**, 92, 1959.

The hydrofluoric acid content of this product may be determined by the current developed on a spontaneous electrolysis of the acid sample, diluted 1:500, between an aluminum anode and a platinum cathode.<sup>36a</sup>

### DETERMINATION OF PHOSPHORIC ACID IN NITRIC ACID

Trace phosphate is not usually determined in nitric acid. Where special interest exists a molybdenum blue photometric method is applicable (with silica being codetermined, if present).<sup>37</sup>

### DETERMINATION OF HYDRIODIC ACID IN NITRIC ACID

Iodide is now seldom encountered in nitric acid; it was formerly determined by oxidation to iodine, extraction, and subsequent titration with thiosulfate.

### DETERMINATION OF RESIDUE ON IGNITION (AND SILICA) IN NITRIC ACID

The determination of the residue on ignition in nitric acid is analogous to that for sulfuric acid (see p. 542). Some workers prefer to determine first the residue on evaporation by taking to dryness on a steam bath and drying completely in an oven at 100°C., then to ignite the residue further to a red heat. Usually, silica is not separately determined in nitric acid. Where a special interest exists, the acid sample is evaporated to dryness in a platinum dish, the residue is dissolved in sodium hydroxide solution, and after appropriate neutralization, a conventional molybdenum blue procedure is applied with phosphate masked by the addition of oxalate or tartrate.<sup>38</sup> (See also Vol. I, pp. 962-963.)

### DETERMINATION OF ARSENIC IN NITRIC ACID

For the determination of trace arsenic in nitric acid, the comments given for the similar determination in sulfuric acid apply (see p. 546). For the Gutzeit method, a known amount of the nitric acid (50 to 100 g.), after addition of 5 ml. of concentrated sulfuric acid and 0.8 g. of  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , is evaporated until no further nitric acid fumes are evolved (i.e., until sulfur trioxide fumes just appear). The general Gutzeit procedure is then applied (see Vol. I, pp. 118-124).

### DETERMINATION OF BORON IN NITRIC ACID

The nuclear industry has interest in the trace boron content of nitric acid. A methyl borate distillation is employed, followed by a photometric determination of borate (Vol. I, pp. 233-235). In one study, special distillation conditions and the use of curcumin as the chromogenic agent have been recommended.<sup>39</sup>

### DETERMINATION OF FREE CHLORINE IN NITRIC ACID

Where of interest, free chlorine may be determined in nitric acid by passing pure air successively through two gas-bubbling bottles (low form), the first contain-

<sup>36a</sup> Baker, B. B., *Anal. Chem.*, **30**, 1085, 1958.

<sup>37</sup> United Kingdom Atomic Energy Authority, P. G. Rept. 69(W), Analytical Methods for the Inspection of Nitric Acid, H. M. Stationery Office, London, 1960.

<sup>38</sup> United Kingdom Atomic Energy Authority, P. G. Rept. 69(W), Analytical Methods for the Inspection of Nitric Acid, H. M. Stationery Office, London, 1960.

<sup>39</sup> United Kingdom Atomic Energy Authority, P. G. Rept. 69(W), Analytical Methods for the Inspection of Nitric Acid, H. M. Stationery Office, London, 1960.

ing the weighed sample of nitric acid, and the second a potassium iodide solution. The iodine liberated in the second bottle is titrated with 0.1 *N* sodium thiosulfate.

$$\% \text{ Free Chlorine} = \frac{(\text{milliliters of Na}_2\text{S}_2\text{O}_3) \times (\text{normality of Na}_2\text{S}_2\text{O}_3) \times 0.03545 \times 100}{\text{sample weight in grams}}$$

### DETERMINATION OF AMMONIUM SALTS IN NITRIC ACID <sup>40</sup>

The determination of small amounts of ammonium salts in nitric acid may be accomplished by a photometric Nessler procedure following an initial evaporation.

**Procedure.**—Transfer a sample of the nitric acid containing 20 to 120  $\mu\text{g}$ . of ammonia to a beaker, add 4 or 5 glass beads, and evaporate on a hot plate until about  $\frac{1}{4}$  in. of acid remains (allow no part of the beaker bottom to go dry). Continue the evaporation on a steam bath just to dryness. Dissolve the cool residue in 64.0 ml. of  $\text{NH}_3$ -free water.

Transfer the solution to a rectangular cell and read the absorbance against water in a filter photometer with a blue filter. Add 1.0 ml. of gum arabic solution (0.2 g. of the gum in 90 ml. of water filtered through a glass wool plug, and 10 ml. of the modified Nessler reagent added to the filtrate as a preservative) and 5.0 ml. of modified Nessler reagent. Stir, taking care not to scratch the cell walls. Allow to stand 5 min. and again determine the absorbance versus water. Run a blank versus water on all of the reagents used in the procedure.

Calculate the net absorbance by subtracting the absorbance of the solution before the addition of the gum arabic and Nessler reagent, and also the absorbance of the reagent blank from the absorbance obtained after the Nesslerization of the sample. Determine the result as percentage of ammonia from a standard curve obtained by adding 0.0, 1.0, 2.0, . . . , 14.0 ml. of standard ammonia solution (0.0314 g. of  $\text{NH}_4\text{Cl}$  dissolved and diluted to exactly 1000 ml. with  $\text{NH}_3$ -free water; 1.0 ml. = 10  $\mu\text{g}$ . of  $\text{NH}_3$ ) to ammonia-free water to a total volume of 64.0 ml., and continue after the second paragraph of the procedure.

**Preparation of Modified Nessler Reagent.**—Add 80 g. reagent grade  $\text{NaCl}$  to a beaker containing 130 ml. of ammonia-free water, and add 100 ml. of saturated  $\text{HgCl}_2$  solution (20 g. of reagent grade  $\text{HgCl}_2$  added to 130 ml. of water, warmed and cooled, stirred to induce crystallization, allowed to settle, and the clear supernatant solution decanted). Mix, and add slowly with vigorous agitation, 70 ml. of 1%  $\text{Li}_2\text{CO}_3$  solution (1 g. reagent grade  $\text{Li}_2\text{CO}_3$  in 100 ml. of water; do not heat to effect solution as an inverse temperature effect exists). Allow the solution to stand overnight in a tightly closed bottle; then filter through an ignited Gooch crucible. The solution will keep indefinitely in a bottle closed with a plastic-lined screw cap.

### DETERMINATION OF IRON IN NITRIC ACID

The determination of iron in nitric acid parallels the procedure given above for sulfuric acid (see p. 549). In both the visual comparison and photometric thiocyanate procedures, a sample corresponding to 5 ml. of concentrated nitric acid is usually appropriate, with the substitution of an equal volume of iron-free nitric acid for the sulfuric acid specified in the standards and blank. For nitric acid

<sup>40</sup> Procedure, courtesy General Chem. Div., Allied Chem. Corp.

low in iron, a preliminary concentration should be effected. An appropriate sample (10 to 50 g.) is evaporated on a steam bath after addition of a few drops of concentrated sulfuric acid. The residue is dissolved in 5 ml. of iron-free nitric acid, diluted with iron-free water and transferred to the 100 ml. Nessler tube (or volumetric flask for the photometric procedure). The solution is then ready for the development of the thiocyanate color without the addition of permanganate.

#### DETERMINATION OF OTHER IMPURITIES IN NITRIC ACID

Some other impurities (e.g., zinc, copper, lead, nickel, and selenium) may be determined, where special interest exists, by the procedures given under sulfuric acid, often after a prior evaporation of a suitable sample with some sulfuric acid added.

#### DETERMINATION OF THE WATER CONTENT OF NITRIC ACID

Where of interest, the water content of concentrated nitric acid may be determined by a direct titration with the Karl Fischer reagent following neutralization with pyridine.<sup>41</sup> The water content of white and red fuming nitric acid is of special interest in its use as a rocket fuel oxidizer. A weighed sample of the white acid is neutralized with pyridine in dimethylformamide, an excess of the Karl Fischer reagent is added, and a back-titration performed to a dead-stop end point with a standard methanol-water solution. Nitrogen dioxide, up to 1.5%, does not interfere.<sup>42</sup> The water content, up to 6%, of red fuming nitric acid, containing up to 20%  $\text{NO}_2$ , can be determined by a highly selective spectrophotometric measurement in the near infrared at  $1.423 \mu$ .<sup>43</sup>

#### SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN NITRIC ACID

As considered above for sulfuric acid (p. 552), the spectrographic determination of impurities at even the level of 0.1 p. p. m. or less, may be accomplished by an initial concentration. The procedure given for sulfuric acid is also applicable to nitric acid (employing 100 g. of nitric acid in place of the 100 g. of sulfuric acid, and proceeding directly to the evaporation). Oldfield and Bridge<sup>44</sup> have reported a detailed spectrographic examination of high purity nitric acid (and also of hydrochloric, hydrofluoric, and acetic acids), and have elected to add copper during the concentration step, which serves as an internal standard. Their original paper is worthy of close study. Their procedure, which permits the estimation of some seventeen elements (namely, Mg, Mn, Cr, Bi, Al, Ni, Mo, Be, In, Zn, Ti, Zr, Co, Fe, Pb, Ga, Cd), takes the following form:

**Spectrographic Procedure with Internal Copper Standard.**—Transfer a 10-ml. sample of the acid ( $\text{HNO}_3$ ,  $\text{HCl}$ , or acetic acid) to a 30-ml. platinum crucible. Add 1 ml. of 0.1  $N$   $\text{H}_2\text{SO}_4$ , and evaporate to dryness. To the cooled crucible add 1.0 ml. of a solution of high-purity grade  $\text{CuSO}_4$  in 0.1  $N$   $\text{H}_2\text{SO}_4$  (1.0 ml. = 1.0 mg. of Cu). Warm the crucible to dissolve the residue, rinse the walls with a little deionized water, and again evaporate to dryness. Dissolve the residue in 0.1 ml. of

<sup>41</sup> Mitchell, J., Jr., and Smith, D. M., *Aquameyry*, Interscience Publishers, Inc., New York, 1948.

<sup>42</sup> Moberg, M. L., Knight, W. P., and Kindsvater, H. M., *Anal. Chem.*, **28**, 412, 1956.

<sup>43</sup> White, L., Jr., and Barrett, W. J., *Anal. Chem.*, **28**, 1538, 1956.

<sup>44</sup> Oldfield, J. H., and Bridge, E. P., *Analyst*, **85**, 97, 1960.

deionized water by warming and rotating the crucible. Transfer the solution dropwise to a heated  $\frac{1}{4}$ -in. undercut graphite electrode (previously pre-arc'd for 4 sec. at 4 amp. to remove surface contamination and to make it porous), allowing each drop to evaporate before adding the next. Rinse the crucible with 0.05 ml. of deionized water and transfer to the electrode in the same manner. Excite this sample preparation in a direct current arc in an argon-oxygen atmosphere at 12 amp. for 15 sec. Develop all plates under identical conditions and compare appropriate line pairs. The concentrations are calculated from working curves obtained by the excitation of prepared standards containing the same amount of copper as the unknowns, and from 0.005 to 5.0  $\mu$ g. of the elements per 0.1 ml. of the solution placed on the electrode.

**Remarks.**—The sensitivity can be further improved by employing a larger sample of the acid. It is imperative that the evaporation steps and transfers be accomplished under conditions where air-borne and other contamination is minimized.

### ANALYSIS OF FUMING NITRIC ACID

In the determinations considered above for nitric acid, only occasional and brief mention is made concerning fuming nitric acid. The special report literature that has developed on this product, associated with its use as a rocket fuel oxidizer, should be consulted for the problems and methods of its analysis.<sup>45</sup>

### ANALYSIS OF REAGENT GRADE NITRIC ACID

For information on the analysis of reagent grade nitric acid and fuming nitric acid, relevant monographs should be consulted (see footnote 27, p. 552).

### HYDROCHLORIC ACID

Hydrochloric acid (muriatic acid), HCl, is available in the technical grade in various strengths including 16°, 18°, 20°, 22°, and 23° Baumé, Heavy (24.6%, 27.9%, 31.4%, 35.2%, and 37.1% HCl), the 18° and 20° Baumé products being the most used. All of these strengths are somewhat yellow in color. A colorless 20° Baumé product is also available. The 18° Baumé acid is also offered with an added metal-corrosion inhibitor for use in pickling iron and steel, and for dissolving hard water scale. Hydrochloric acid is available in a pharmaceutical grade, 35 to 38% HCl, meeting the specifications of the U. S. Pharmacopeia. Reagent grade (arsenic-free) hydrochloric acid, meeting American Chemical Society Specifications, contains 36.5 to 38.0% HCl (typically 37.2%, sp. gr. 1.19). A specific gravity-composition table for hydrochloric acid appears on page 621. Anhydrous liquid hydrogen chloride is available in cylinders; for the analysis of this product, initial absorption in potassium hydroxide solution is employed.

### HYDROCHLORIC ACID CONTENT

**Hydrochloric Acid Content by Specific Gravity.**—The estimation of the hydrochloric acid content by the use of a hydrometer is feasible over the entire range of

<sup>45</sup> For brief summary, see Clear, A. J., and Roth, M., Nitrogen, in Kolthoff, I. M., and Elving, P. J., eds., *Treatise on Analytical Chemistry*, Interscience Publishers, Inc., New York, Part II, Vol. 5, 1961, 264-267; see also Clark, J. D., Streim, H. G., et al., U. S. Naval Air Rocket Test Station, Lake Denmark, New Jersey, *Analytical Procedures for Rocket Propellants*, Reports 20, 23, 24, and 34, 1951-1953; U. S. Military Specification, MIL-N-7254C, Nitric Acid, Fuming, Technical, July, 1956.

practical concentrations of hydrochloric acid. A specific gravity-composition table for hydrochloric acid is given on page 621.

**Hydrochloric Acid Content by Alkalimetric Titration.**—The procedure for the determination of the total acidity of hydrochloric acid by acid-base titrimetry parallels that given above for sulfuric acid (p. 540), and needs only a brief statement here.

**Procedure.**—Because of the volatility of hydrogen chloride, employ precautions to avoid losses in establishing the acid sample. Use a weighing bottle or a Dely or snake tube; with such tubes, draw the sample into the tube slowly under only slight suction. Use a chamber buret (see footnote 3, p. 536) and a sample size requiring 75 to 95 ml. of 0.5 *N* NaOH (3.2 to 4.0 ml. of 37.2% HCl). Run about 75 ml. of the base into the casserole or conical flask, and only then add the weighed acid sample. Complete the titration to the methyl orange or methyl red end point or, alternatively, employ a potentiometric end point. Note the temperature of the NaOH solution and add a correction of 0.00030 ml. per milliliter of 0.5 *N* NaOH for each degree Centigrade below its standardization temperature; or subtract the correction for each degree above.

**Calculation.**

% Total Acidity as HCl

$$= \frac{(\text{milliliters of NaOH}) \times (\text{normality of NaOH}) \times 0.036461 \times 100}{\text{sample weight in grams}},$$

where the volume of NaOH is corrected for temperature.

If the sample contains significant amounts of other acids, a correction may be applied following their determination. For example

$$\% \text{ HCl} = \text{Total Acidity as HCl} - (\% \text{ HNO}_3 \times 0.5786) - \% \text{ H}_2\text{SO}_4 \times (0.7435).$$

**Remarks.**—The hydrochloric acid content may also be determined gravimetrically as AgCl or by a Volhard titration (Vol. I, pp. 328–329).

## DETERMINATION OF SULFURIC ACID IN HYDROCHLORIC ACID

Sulfuric acid in hydrochloric acid can be determined after the procedures described above for nitric acid (see p. 560). The initial acid sample is evaporated to the absence of a hydrogen chloride odor, the beaker walls are rinsed with water, and the solution is re-evaporated. The result of the subsequent alkalimetric titration is termed % Free  $\text{H}_2\text{SO}_4$  or % Nonvolatile Acidity as  $\text{H}_2\text{SO}_4$ , or may be given as % Free Sulfate as  $\text{SO}_3$  (or  $\text{SO}_4$ ). If total sulfate is determined (i.e., the total of sulfate as sulfuric acid "bound" by metals) either gravimetrically or turbidimetrically the result is usually termed percentage of total sulfate, and is expressed as  $\text{SO}_3$ , per cent or  $\text{SO}_4$ , per cent. For trace sulfate in high purity hydrochloric acid (and certain other chemicals including phosphoric acid, acetic acid, and sodium carbonate), a sulfide evolution method is promising. The sample is treated with a titanium-phosphoric acid reagent. The hydrogen sulfide formed by reduction is swept by carbon dioxide into sodium hydroxide solution, and is then titrated with mercury(II) acetate to the dithizone end point. Amounts down to 10  $\mu\text{g}$ . of sulfate may thus be determined.<sup>46</sup>

<sup>46</sup> Quartermain, P. G., and Hill, A. G., *Analyst*, **85**, 211, 1960.



### DETERMINATION OF NITRIC ACID (OR NITRATE) IN HYDROCHLORIC ACID

The methods for nitric acid or nitrate in sulfuric acid (p. 543) are directly applicable to hydrochloric acid. As the determinations are effected in a sulfuric acid medium, a suitable sample of the hydrochloric acid (5 ml. of concentrated acid) is added under the surface of 75 ml. of reagent grade sulfuric acid. This required dilution reduces the sensitivity of the procedures accordingly.

### PHOSPHORIC ACID IN HYDROCHLORIC ACID

Phosphate in hydrochloric acid, where of special interest, may be determined by a conventional molybdenum blue procedure using tin(II) chloride as the reductant following a preliminary evaporation of a 10-g. sample of the acid with 3 ml. of water added to assure the absence of spitting.<sup>47</sup>

### DETERMINATION OF RESIDUE ON IGNITION AND SILICA IN HYDROCHLORIC ACID

In hydrochloric acid, the residue on evaporation and the residue on ignition are determined in the same manner as for nitric acid (see p. 563). Where of interest, silica is determined by treatment of the ignited residue with hydrofluoric acid, evaporation, and reweighing.

**Procedure for Silica in Hydrochloric Acid.**—To the platinum dish containing the ignited and weighed residue of the acid, add 5 ml. of reagent grade HF and a few drops of concentrated  $H_2SO_4$ . Evaporate to dryness, ignite at a red heat, and reweigh. The loss in weight corresponds to  $SiO_2$ .

$$\% SiO_2 = \frac{(\text{loss in weight in grams on HF treatment}) \times 100}{\text{sample weight in grams}}$$

### DETERMINATION OF ARSENIC IN HYDROCHLORIC ACID

The methods and references above, relating to the determination of arsenic in sulfuric acid (p. 546) are pertinent to the determination of this element in hydrochloric acid. For the Gutzeit method, a known amount of this acid (25 to 50 g.), after addition of 0.5 ml. of concentrated nitric acid (to assure retention of arsenic) and 0.8 g. of  $FeNH_4(SO_4)_2 \cdot 12H_2O$ , is evaporated on a hot plate until no further hydrogen chloride is evolved, and just to the appearance of sulfur trioxide fumes. The general Gutzeit procedure is then applied (see Vol. I, pp. 118–124).

### DETERMINATION OF IRON IN HYDROCHLORIC ACID

The determination of iron in hydrochloric acid parallels the thiocyanate procedures for iron in sulfuric acid (see p. 549), following the evaporation of hydrochloric acid (completed on a steam bath to assure a soluble residue and with sodium carbonate added). Often 10 ml. of 1:1 sulfuric acid are added to 100 g. of the hydrochloric acid (or another amount, depending on the iron content) and the solution is evaporated to strong sulfur trioxide fumes. The residual solution is then transferred to a 100-ml. volumetric flask (or Nessler tube) with water rinses.

<sup>47</sup> United Kingdom Atomic Energy Authority, P. G. Rept. 76(W), Analytical Methods for the Inspection of Hydrochloric Acid, H. M. Stationary Office, London, 1960.

(The volume is then about 60 ml.) The thiocyanate procedures given for sulfuric acid are thereupon followed (p. 549). Where the residue on ignition has been determined, the residue may be digested with about 5 ml. of 1:1 hydrochloric acid (with the dish covered with a watch glass), then evaporated to dryness, taken up in about 35 ml. of 1:6 hydrochloric acid and 10 ml. of 1:1 sulfuric acid, and evaporated until the volatilization of hydrogen chloride is complete (*not* to sulfur trioxide fumes). The residual solution is transferred as above

### DETERMINATION OF FREE CHLORINE IN HYDROCHLORIC ACID

The examination of free chlorine in hydrochloric acid may range from a limit test to a quantitative determination, depending on the amount of chlorine present and the grade of the acid. Two general approaches are utilized: oxidation of iodide to iodine and evaluation of its color or its titration with thiosulfate; or evaluation of the color developed by the reaction of *o*-tolidine with the free chlorine. It is imperative that water used for dilution and glassware be free of a "demand" for free chlorine (see remarks, Vol. I, p. 335).

**Procedure for Free Chlorine Based on Iodometric Titration.**<sup>48</sup>—Transfer a 50-ml. sample of the (concentrated) HCl to a 250-ml., glass-stoppered conical flask. Add 50 ml. of water. Cool the solution to below 25°C. in order to secure a satisfactory end point. Add 5 ml. of 1% KI solution (1 g. of KI in 100 ml. of water with 2 drops of 0.1 *N* NaOH added to obviate aerial oxidation of iodide). (The relatively small amount of KI used reduces any iron interference.) Stopper the flask, mix, and allow to stand 1 min. Add starch indicator, and titrate to the disappearance of the blue color with 0.01 *N* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

$$\% \text{ Free Chlorine} = \frac{(\text{milliliters of Na}_2\text{S}_2\text{O}_3) \times (\text{normality of Na}_2\text{S}_2\text{O}_3) \times 0.03545 \times 100}{\text{weight of sample in grams}}$$

**Remarks.**—In routine analysis, it is probably best to standardize the 0.01 *N* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> against weighed amounts of iodine under the conditions of this titration.

**Visual Procedure for Free Chlorine Based on Iodide Oxidation.**—Add a 20-ml. sample of the (concentrated) HCl to 40 ml. of water, cooled to 4 to 6°C., contained in a 250-ml. beaker. Add 10 ml. of a KI-starch reagent (0.4 g. soluble starch and 7 ml. cold water slurried, diluted to 100 ml. with boiling water, cooled, 0.2 g. of KI added and stirred to dissolve; store in a glass-stoppered, brown bottle for a maximum of 3 days). No blue color should develop in 10 min. (compared with equal volume of water) against a white background under diffuse illumination. In absence of color, the free chlorine corresponds to 0.00001% or less.

**Remarks.**—Such iodine procedures can be made semiquantitative by the use of standards prepared from a stock sodium hypochlorite solution. Iron can be masked (if present at greater than 0.00001%) by the addition of pyrophosphate ion. A further limit test is based on the omission of the starch and extraction of any iodine formed into a 1-ml. layer of CS<sub>2</sub>.

**Procedure for Free Chlorine Employing *o*-Tolidine.**<sup>49</sup>—Add a 25-ml. sample of (concentrated) HCl to a 250-ml. beaker containing 60–70 ml. of water cooled to 4 to 6°C. by a water-ice bath. Transfer to a 100-ml. Nessler tube. Adjust the

<sup>48</sup> Procedure, courtesy, General Chem. Div., Allied Chem. Corp.

<sup>49</sup> Procedure, courtesy, E. I. DuPont de Nemours & Co., Inc.

temperature to 20 to 25°C., introduce by a pipet 5 ml. of *o*-tolidine reagent (0.5 g. of *o*-tolidine hydrochloride ground to a paste in a mortar with 2.5 ml. of HCl (1:4), transferred to a 500-ml. graduated cylinder, diluted to 250 ml. with water, and then to 500 ml. with HCl (1:4); store away from direct sunlight in a glass-stoppered brown bottle, and discard after 5 months). Compare the sample preparation within 30 min. with a series of permanent color standards in matched Nessler tubes, by looking down through the solutions against a white background diffusely illuminated (avoid direct sunlight since it fades the sample preparation).

The permanent standards consist of mixtures of the volumes specified below of Solution *A* (2.5 g. of  $K_2Cr_2O_7$ , 1 ml. concentrated  $H_2SO_4$ , diluted to 1000 ml. with water) and Solution *B* (1.5 g.  $CuSO_4 \cdot 5H_2O$ , 1 ml. of concentrated  $H_2SO_4$ , diluted to 100 ml. with water) diluted to 100 ml. with water, and stored in glass-stoppered bottles. In use, Nessler tubes are filled with the standards to the same depth as the sample preparation.

Equivalent free chlorine, 25-ml. sample		Standard mixture diluted to 100 ml.	
% Free $Cl_2$	p. p. m. free $Cl_2$	Solution <i>A</i> , ml.	Solution <i>B</i> , ml.
0.0003	3	9	8
0.0006	6	16	8
0.0009	9	22	8
0.0012	12	28	8

The standards may be checked by comparison with portions of a stock sodium hypochlorite solution, suitably diluted and adjusted in acidity, carried through the procedure; the range of the standards may be thus extended.

Remarks.—Photometric or spectrophotometric *o*-tolidine procedures are also possible, which are similar to those employed for available chlorine in water (see Vol. I, pp. 334 and 335), but substituting the above *o*-tolidine reagent, since the HCl sample provides some of the required acidity.

### DETERMINATION OF OTHER IMPURITIES IN HYDROCHLORIC ACID

Other impurities, for example, "heavy metals," zinc, copper, nickel, and lead, in hydrochloric acid, if of interest, may usually be determined by the methods given above under sulfuric acid. In general, the sample of the acid is initially evaporated after addition of concentrated sulfuric acid. Boron may be determined by the photometric method noted under nitric acid (see p. 563).<sup>50</sup> The spectrographic procedures for trace impurities in high purity nitric acid are directly applicable to hydrochloric acid (see p. 565).

<sup>50</sup> United Kingdom Atomic Energy Authority, P. G. Rept. 76(W), Analytical Methods for the Inspection of Hydrochloric Acid, H. M. Stationery Office, London, 1960.

ANALYSIS OF REAGENT AND PHARMACEUTICAL GRADE  
HYDROCHLORIC ACID

For information on the analysis of reagent grade and pharmaceutical grade hydrochloric acid, relevant monographs should be consulted.<sup>51</sup>

## PERCHLORIC ACID

Perchloric acid,  $\text{HClO}_4$ , in the technical grade is predominantly offered in the 70–72% strength. The U. S. Interstate Commerce Commission prohibits the shipment of perchloric acid in excess of 72% concentration. The total acidity of the product is usually determined by a direct titration with 1 N sodium hydroxide to the phenolphthalein end point. Impurities commonly determined include residue on ignition, chloride, nitrogen compounds, sulfate, heavy metals, and iron; determinations are by the conventional procedures without interference by the perchlorate anion. In certain of these determinations the perchloric acid sample is initially evaporated to dryness. Where of interest, silica (and phosphate) may be determined by a conventional molybdenum blue photometric procedure. Reagent grade perchloric acid, meeting American Chemical Society specifications, is available in 60 to 62% (sp. gr. 1.54) and 70 to 72% (sp. gr. 1.70) strengths, with most of the above mentioned impurities controlled.<sup>52</sup> Reagent grade material meeting the British Analar standards also includes limit tests for lead, copper, manganese, ammonium, arsenic, and chlorate.<sup>53</sup> For additional information on perchloric acid, including the density of solutions, the special literature should be consulted.<sup>54</sup>

## CHLOROSULFONIC ACID

Chlorosulfonic acid,  $\text{ClSO}_3\text{H}$ , is commercially available in bulk quantities, in an approximate strength of 62.3° Baumé, Heavy (minimum 98.5%  $\text{ClSO}_3\text{H}$ ). Typically the product may contain 98.8% total  $\text{ClSO}_3\text{H}$ ; total sulfate as  $\text{SO}_3$ , 69.0%; total chloride as  $\text{HCl}$ , 30.9%; sulfuric acid, 0.7%, and free sulfur trioxide as  $\text{SO}_3$ , 0.6%.

DETERMINATION OF THE CONSTITUENTS OF  
CHLOROSULFONIC ACID

The establishment of the composition of chlorosulfonic acid may be based on the titration of the total acidity, followed by the determination of the chloride content of the resulting solution by a precipitation titration with silver (potentiometric or Mohr end point). The results of these titrations are expressed as percentage of  $\text{SO}_3$  and percentage of  $\text{HCl}$ , and the excess of  $\text{SO}_3$  beyond the stoichiometry  $\text{SO}_3 + \text{HCl} = \text{ClSO}_3\text{H}$  is expressed as percentage of free  $\text{SO}_3$ . This indirect determination of free sulfur trioxide, however, often leads to a quite imprecise result because the small difference between two large numbers is involved. Although the situation may be improved slightly by a gravimetric determination of total chloride,

<sup>51</sup> U. S. Pharmacopeia; British Pharmacopœia; also see footnote 27, p. 552.

<sup>52</sup> American Chemical Society, Reagent Chemicals—1960, Washington, D. C., 1961.

<sup>53</sup> British Drug Houses Ltd. and Hopkin & Williams Ltd., Analar Standards for Laboratory Chemicals, London, 5th Ed., 1957.

<sup>54</sup> Schumacher, J. C., ed., Perchlorates: Their Properties, Manufacture and Uses, Reinhold Publishing Corp., New York, 1960.

the preferred practice is to employ a temperature-rise method, based on the reaction of the free sulfur trioxide with added hydrogen chloride to form chlorosulfonic acid.

**Procedure for Total Acidity and Chloride Content.**—Place about 75 ml. of 0.333 . . . *N* NaOH from a chamber buret (see footnote 3, p. 536) in a casserole or glass-stoppered conical flask. Add the weighed  $\text{ClSO}_3\text{H}$  sample (sufficient to consume about 85 ml. of the 0.333 . . . *N* NaOH) via a Dely tube or a sealed glass bulb or ampoule. Continue the titration to the methyl orange end point, or employ a potentiometric end point. Note the temperature of the NaOH solution, and add a correction of 0.00028 ml. per milliliter of 0.333 . . . *N* NaOH added for each degree Centigrade below its standardization temperature; or subtract the correction for each degree above.

Titrate the resulting solution with 0.1 *N*  $\text{AgNO}_3$  to a potentiometric end point (silver wire-calomel electrode pair) or conduct a conventional Mohr titration following the addition of 2 g. of  $\text{NaHCO}_3$  (see Vol. I, pp. 332–333). For either titration technique, establish a blank by titrating a similar amount of the 0.333 . . . *N* NaOH, neutralized appropriately with chloride-free  $\text{H}_2\text{SO}_4$ , with 0.1 *N*  $\text{AgNO}_3$ . (For calculation of results see below.)

**Procedure for Free Sulfur Trioxide (Temperature Rise Method).**<sup>55</sup>—Employ the apparatus shown in Fig. 22-5. Dry thoroughly the Dewar flask and stopper, *F*, containing the disperser, inlet and outlet tubes, at 105–110°C. in an oven. Transfer to a desiccator and allow to cool. Assemble the fore part of the train, as illustrated, and pass anhydrous HCl until all air is swept out (3 to 5 min.), allowing the gas to escape to a hood at the exit from the drying tube, *E*. Stop the flow of HCl from the cylinder, and clamp shut the tubing leaving the drying tube. Insert the thermometer, *H*, in the Dewar flask stopper, add 35 ml. of the  $\text{ClSO}_3\text{H}$  sample to the Dewar flask (i.e., to a calibration mark on the flask wall), position the stopper firmly in place, and connect the inlet tube of this flask to the exit tube of the drying tube. Record the temperature of the sample to the nearest 0.1°C. Start a slow stream of HCl gas through the train (1 to 3 bubbles per sec. in the  $\text{H}_2\text{SO}_4$ -filled flask, *D*). Note the maximum temperature developed in a short time, and persisting for possibly a minute. (The rate of the temperature rise and the maximum temperature developed increases with the free  $\text{SO}_3$  content, and the time the maximum temperature is maintained decreases.)

**Calculation.**

$$\% \text{ Free (Uncombined) SO}_3 = (T_{\text{max}} - T_0) \times 0.291$$

where  $T_{\text{max}}$  and  $T_0$  are the maximum and initial temperatures, respectively. The factor 0.291 strictly applies to a definite sample size and to apparatus of fixed heat transfer properties; however, the factor can be used for most Dewar flasks with an error of only a few per cent relative. For higher accuracy the apparatus should be calibrated against  $\text{ClSO}_3\text{H}$  with known amounts of  $\text{SO}_3$  added.

**Remarks.**—Moisture must be excluded from the sample during the determination. The  $\text{H}_2\text{SO}_4$  and  $\text{CaSO}_4$  drying agents should be renewed frequently (every 2 weeks). When not in use the HCl cylinder should be disconnected and its outlet fitted with a drying tube; further, the entrance and exit to the train should be protected by drying tubes. The sample size is probably most expeditiously estab-

<sup>55</sup> Seaman, W., Woods, J. T., Bank, H. N., *Anal. Chem.*, **22**, 549, 1950, modified procedure and apparatus description, courtesy, E. I. DuPont de Nemours & Co., Inc.

lished by placing a calibration mark on the wall of the Dewar flask. Prior to a run, the entire train, with the HCl gas cylinder and also the acid sample, should be placed in a hood for a sufficient time to allow temperature equilibration. If the HCl gas entering the sample is not at the same temperature, the results obtained may not be consistent. If the  $\text{ClSO}_3\text{H}$  (process) sample contains large amounts of  $\text{SO}_3$  (possibly greater than 3%), it may be necessary to dilute with  $\text{ClSO}_3\text{H}$  of known low free  $\text{SO}_3$  content, as otherwise too large an amount of HCl is required.

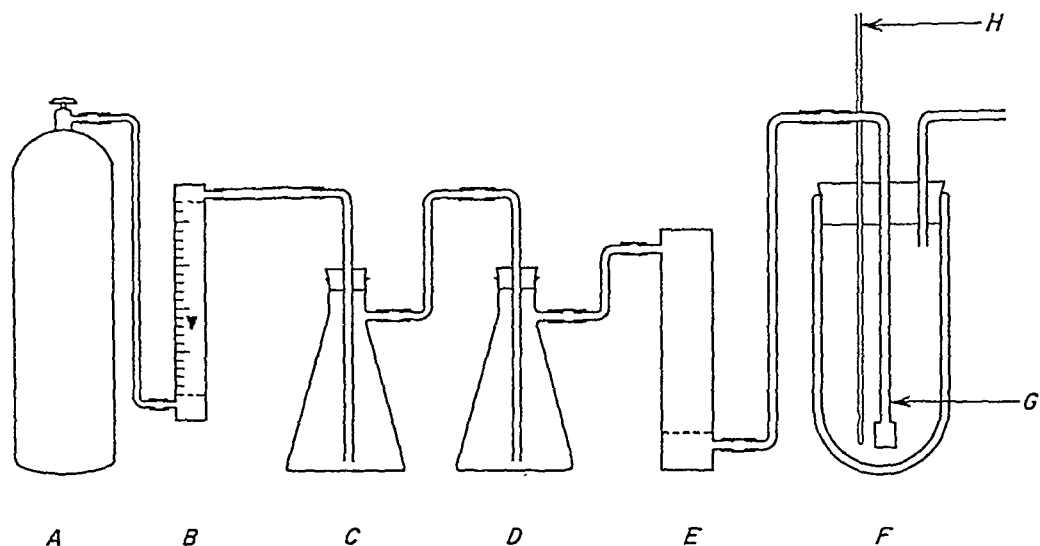


FIG. 22-5. Apparatus for Determination of Free  $\text{SO}_3$  in Chlorosulfonic Acid: A, cylinder, anhydrous HCl; B, float gas flowmeter; C, 1000-ml. filter flask, dry trap; D, 1000-ml. filter flask containing reagent grade  $\text{H}_2\text{SO}_4$ ; E, drying tube filled with anhydrous  $\text{CaSO}_4$ ; F, 25-mm. by 100-mm. Dewar flask; G, fritted glass gas disperser; H, thermometer,  $20^\circ$  to  $40^\circ\text{C}$ .,  $0.1^\circ$  divisions.

For the determination of free HCl in  $\text{ClSO}_3\text{H}$  by its volatilization at reduced pressure, the paper of Korinith should be consulted.<sup>56</sup>

**Calculation of the Composition of Chlorosulfonic Acid.**—This is based on the results of the titrations of total acidity and total chloride content and the determination of the free sulfur trioxide by the temperature rise method. From the first titration

% Total Acidity expressed as  $\text{SO}_3$

$$= \frac{(\text{milliliters of NaOH}) \times (\text{normality of NaOH}) \times 0.040031 \times 100}{\text{sample weight in grams}}$$

where the volume of NaOH is corrected for temperature. From the second titration

$$\% \text{ Total chloride as HCl} = \frac{(V - v) \times (\text{normality of AgNO}_3) \times 0.03646 \times 100}{\text{sample weight in grams}}$$

where  $V$  and  $v$  are milliliters of  $\text{AgNO}_3$  required by the sample and blank respectively. Since the commercial product has free  $\text{SO}_3$ , the actual  $\text{ClSO}_3\text{H}$  present is

<sup>56</sup> Korinith, E., *Angew. Chem.*, 72, 108, 1960.

calculated from the total chloride content (the free chloride content being negligible). Hence  $\% \text{ClSO}_3\text{H} = \% \text{Total Chloride as HCl} \times 3.1958$ . To calculate the total sulfate it is necessary to deduct the acidity due to HCl, suitably expressed, from the total acidity:  $\% \text{Total Sulfate as SO}_3 = \% \text{Total Acidity as SO}_3 - \% \text{Total Chloride as HCl} \times 1.0979$ . The free  $\text{H}_2\text{SO}_4$  can then be estimated from the following stoichiometry:  $\% \text{Free H}_2\text{SO}_4 = (\% \text{Total Sulfate as SO}_3 - \% \text{ClSO}_3\text{H} \times 0.6871 - \% \text{Free SO}_3) \times 1.2250$ . Composition values usually reported include  $\% \text{ClSO}_3\text{H}$ ,  $\% \text{Total Sulfate as SO}_3$ ,  $\% \text{Free SO}_3$ ,  $\% \text{Total Chloride as HCl}$ , and  $\% \text{Free H}_2\text{SO}_4$ .

### DETERMINATION OF IRON IN CHLOROSULFONIC ACID

The determination of iron in chlorosulfonic acid parallels the visual comparison and photometric procedures given above for sulfuric acid (p. 549), following an initial evaporation. Typically, 40 or 50 ml. of the chlorosulfonic acid and 8 or 10 ml. of iron-free sulfuric acid (1:1) are evaporated in a beaker to a volume of 5 to 10 ml., or to the appearance of turbidity. After cooling, the beaker walls are washed with water and the solution is evaporated to sulfur trioxide fumes. The cooled contents of the beaker are transferred to a 100-ml. volumetric flask (or Nessler tube) with water rinses. The thiocyanate procedures given for sulfuric acid are thereupon followed (p. 549).

### OTHER IMPURITIES IN CHLOROSULFONIC ACID

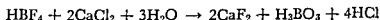
Where of interest, other impurities in chlorosulfonic acid may be determined by the procedures given for hydrochloric or sulfuric acids, often after an initial evaporation.

### FLUOBORIC ACID

Fluoboric acid (tetrafluoroboric acid),  $\text{HBF}_4$ , is offered in 48% nominal strength, and is receiving increasing commercial attention, especially in electroplating.

### DETERMINATION OF THE COMPOSITION OF FLUOBORIC ACID

The composition of fluoboric acid is usually determined by its hydrolysis under reflux in the presence of calcium chloride. The overall reaction is



The strong acid content is titrated with sodium hydroxide, added in part during the hydrolysis. Mannitol is then added and the boric acid content determined by titration with sodium hydroxide. From the stoichiometry involved, the percentage of  $\text{HBF}_4$  can be calculated and either the percentage of free  $\text{H}_3\text{BO}_3$  or the percentage of free HF present. In the usual commercial product, the boric acid is in excess (about 3%).

**Procedure.**<sup>57</sup>—In a platinum thimble, weigh a 2-g. sample of  $\text{HBF}_4$  and transfer with water rinses to a 500-ml. conical flask with a standard taper joint. Add 25 g. of  $\text{CaCl}_2$ , 2 drops of methyl orange solution, 3 to 5 drops of octanol (as an anti-foaming agent), and several boiling chips or beads. Attach the flask to a vertically mounted Liebig condenser, and heat the solution to boiling. From a buret

<sup>57</sup> Procedure, courtesy, General Chem. Division, Allied Chem. Corp.

mounted above the condenser, slowly add 1 N NaOH to the refluxing solution so that the methyl orange just exhibits its acid color. (If the solution is accidentally brought to the alkaline side and does not promptly become acid on further reflux, add some 1 N  $\text{H}_2\text{SO}_4$  and apply a correction to the base consumed.) Reflux for 15 more min. after the last addition of base; then cool the flask and contents with the condenser in place by immersion in a water bath. Wash down the condenser walls with water. Remove the condenser and complete the titration of the cooled hydrolysis mixture with the 1 N NaOH to the methyl orange end point. Record the milliliters required,  $V_1$ . Now add about 35 g. of mannitol (preneutralized, if necessary) and some phenolphthalein indicator. Titrate with 1 N NaOH to an end point persisting for at least 30 sec. Record the milliliters required,  $V_2$ .

**Calculation.**—In this simple scheme acids other than  $\text{HBF}_4$  and either HF or  $\text{H}_3\text{BO}_3$  are assumed to be absent (or to be present in negligible amounts). The result of the first titration step, namely, the total acidity in hot solution, is given by

$$\% \text{ Total Acidity (hot) as } \text{HBF}_4 = \frac{(V_1) \times (\text{normality of NaOH}) \times 0.021953 \times 100}{\text{weight of sample in grams}}$$

The result of the second titration step, namely, the total boric acid content, for calculation purposes is expressed as  $\text{HBF}_4$ :

$$\% \text{ Total } \text{H}_3\text{BO}_3 \text{ expressed as } \text{HBF}_4 = \frac{(V_2) \times (\text{normality of NaOH}) \times 0.08781 \times 100}{\text{weight of sample in grams}}$$

The *lower* of these two percentages is reported as the  $\text{HBF}_4$  content. If the second percentage is *greater* than the first, as is usual for the commercial product, report the difference as  $\% \text{ Free } \text{H}_3\text{BO}_3 = (\% \text{ Total } \text{H}_3\text{BO}_3 \text{ expressed as } \text{HBF}_4 - \% \text{ Total Acidity (hot) as } \text{HBF}_4) \times 0.7042$ . If the second percentage is the *smaller*, report the difference as  $\% \text{ Free HF} = (\% \text{ Total Acidity (hot) as } \text{HBF}_4 - \% \text{ Total } \text{H}_3\text{BO}_3 \text{ expressed as } \text{HBF}_4) \times 0.9113$ .

The percentage of  $\text{HBF}_4$  here determined neglects any acidity due to the presence of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SiF}_6$ . If these are determined, a correction can be applied (see below).

A more sophisticated scheme for the analysis of fluoboric acid has been devised<sup>58</sup> in which the fluosilicic acid and sulfuric acid contents are determined, and a correction is applied to the fluoboric acid content, determined by a procedure essentially similar to that given above. The consideration is here limited to the usual case where free boric acid, rather than free hydrofluoric acid, is present.

**Procedure for Sulfuric Acid.**—Evaporate a 10.0-g. sample of the  $\text{HBF}_4$  in a platinum dish on a steam bath until white fumes cease (about 2 hr.). Add 10 ml. of water and evaporate. Repeat the addition of water and the evaporation until the vapor no longer has the pungent odor characteristic of  $\text{HBF}_4$ . Add 25 ml. of water and titrate with 0.5 N NaOH to the phenolphthalein end point.

$$\% \text{ H}_2\text{SO}_4 = \frac{(\text{milliliters of NaOH}) \times (\text{normality of NaOH}) \times 0.04904 \times 100}{\text{weight of sample in grams}}$$

<sup>58</sup> Flisik, H., Swinehart, C. F., and Bumblis, A. R., Harshaw Chem. Co.; for full details see Booth, H. S., and Martin, D. R., *Boron Trifluoride and Its Derivatives*, John Wiley and Sons, New York, 1949, 230–238.



**Remarks.**—If the residue is solid, as is the case if the  $\text{HBF}_4$  has been allowed to stand for protracted periods in contact with glass, sodium and other metal, salts are present and the determination of sulfuric acid fails. In such a case, the percentage of total solids may be determined by weighing the final residue after drying at  $105^\circ\text{C}$ . in an oven.

**Procedure for Fluosilicic Acid.**—Weigh and transfer a 2-g. sample of the acid into a 150-ml. beaker with 25 ml. of water; add 1 g. of solid  $\text{KNO}_3$ , stir to dissolve, and add 30 ml. of ethanol or 2-propanol. Stir, cover the beaker, allow to stand for 1 hr. Filter the precipitate of  $\text{K}_2\text{SiF}_6$  and  $\text{KBF}_4$  through a Gooch crucible or paper. Wash the precipitate with (1:1) portions of ethanol-water or 2-propanol-water containing 2%  $\text{KNO}_3$  and made alkaline (faint pink color with phenolphthalein). Continue until the further washing is free of acidity (one drop of 0.1  $N$   $\text{NaOH}$  produces pink color with phenolphthalein). Place the crucible or paper in the original beaker, add 100 ml. of water, heat to  $40^\circ\text{C}$ . (and not above  $50^\circ\text{C}$ .) until the precipitate dissolves (and  $\text{H}_2\text{SiF}_6$  only is hydrolyzed). Titrate with 0.5  $N$   $\text{NaOH}$  to the phenolphthalein end point (faint pink persisting for 15 sec.). The titration results correspond to 4 of the 6 fluorine atoms in  $\text{H}_2\text{SiF}_6$ .

$$\% \text{H}_2\text{SiF}_6 = \frac{(\text{milliliters of NaOH}) \times (\text{normality of NaOH}) \times 0.03602 \times 100}{\text{sample weight in grams}}$$

This procedure may give slightly high results.

**Calculations.**—From the initial determinations, values are known for % Total Acidity (hot) as  $\text{HBF}_4$  and for % Total  $\text{H}_3\text{BO}_3$  expressed as  $\text{HBF}_4$  (see "Calculations," on p. 575). From the independent determinations given above, values for %  $\text{H}_2\text{SO}_4$  and %  $\text{H}_2\text{SiF}_6$  are obtained; these last percentages are reported. In addition, the actual percentage of  $\text{HBF}_4$  and actual percentage of Free  $\text{H}_3\text{BO}_3$  are calculated as follows and reported: the Actual %  $\text{HBF}_4$  = % Total Acidity (hot) as  $\text{HBF}_4$  - %  $\text{H}_2\text{SO}_4 \times 0.4477$  - %  $\text{H}_2\text{SiF}_6 \times 0.9141$ . Actual % Free  $\text{H}_3\text{BO}_3$  = (% Total  $\text{H}_3\text{BO}_3$  expressed as  $\text{HBF}_4$  - Actual %  $\text{HBF}_4$ )  $\times 0.7042$ . (These two calculations apply in the usual case where the product contains free  $\text{H}_3\text{BO}_3$ ; where free  $\text{HF}$  is present, analogous equations may be derived from the stoichiometry involved.)

### DETERMINATION OF CHLORIDE IN FLUOBORIC ACID

Where of interest, trace chloride in fluoboric acid may be determined turbidimetrically essentially after the procedure described for nitric acid (see p. 561).

### DETERMINATION OF LEAD AND COPPER IN FLUOBORIC ACID

Where of interest, lead may be determined in fluoboric acid turbidimetrically as lead sulfide (essentially by the procedure in Vol. I, pages 573-576) after repeated evaporations with hydrochloric acid additions. Copper may be determined after the procedures given for this metal in sulfuric acid (page 551) following an initial evaporation with sulfuric acid added.

### SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN FLUOBORIC ACID

For the spectrographic examination of fluoboric acid, the following technique of sample preparation is expedient as contamination from glass, and the addition of

artifacts from the neutralizing base are avoided by use of aerial diffusion of ammonia.<sup>59</sup>

**Procedure.**—Pipet aliquots of the fluoboric acid into two small polyethylene vessels (e.g., slip-on caps for vials, 16-mm. diameter, 8-mm. depth). Transfer the filled vessels, and also a crucible containing aqua ammonia, to a desiccator or other suitable closed container. Allow to stand until one aliquot is found to be alkaline to indicator paper; discard this aliquot. Place the second aliquot under an infrared lamp; bring to dryness, and transfer the entire residue to the graphite electrode, and proceed with the spectrographic excitation (see pp. 552 and 565). Discard the polyethylene vessels.

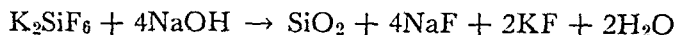
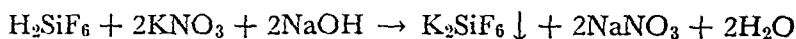
**Remark.**—This elegant neutralization technique is applicable to other acidic solutions. Some workers prefer to use a cup electrode without prior neutralization or evaporation of the fluoboric acid sample.

## FLUOSILICIC ACID

Fluosilicic acid (fluorosilicic acid, hydrofluorosilicic acid, hydrofluosilicic acid, hexafluorosilicic acid, silicofluoric acid),  $\text{H}_2\text{SiF}_6$ , is offered commercially usually as a 30% aqueous solution (sp. gr. 1.27) and also in a reagent grade (30 to 32%  $\text{H}_2\text{SiF}_6$ ).

### FLUOSILICIC ACID CONTENT

The determination of the fluosilicic acid content of fluosilicic acid is often based on hydrolysis of the acid and titration with sodium hydroxide.



**Procedure.**<sup>60</sup>—Add a suitable sample of  $\text{H}_2\text{SiF}_6$  (3 g.) to 25 ml. of ice-cold water in a 150-ml. beaker. Add 1 g. of solid  $\text{KNO}_3$ , stir to dissolve, and add 30 ml. of ice-cold ethanol. Cool in an ice-water bath and titrate rapidly with 1 N NaOH to the phenolphthalein end point. Record the volume of NaOH consumed (and correct for its temperature in the buret).

% Total Acidity as  $\text{H}_2\text{SiF}_6$

$$= \frac{(\text{milliliters of NaOH}) \times (\text{normality of NaOH}) \times 0.072046 \times 100}{\text{sample weight in grams}},$$

where the volume of NaOH is corrected for temperature.

Now heat the solution to 80°C. and titrate further with 1 N NaOH. Record the volume of NaOH consumed in the second titration (and correct for its temperature in the buret).

$$\% \text{ Total } \text{H}_2\text{SiF}_6 = \frac{(\text{milliliters of NaOH}) \times (\text{normality of NaOH}) \times 0.036023 \times 100}{\text{sample weight in grams}},$$

where the volume of NaOH is corrected for temperature.

If no other acids are present, the consumption of NaOH in the second titration

<sup>59</sup> Murt, E. M., and Manns, T. J., *Chemist-Analyst*, 50, 13, 1961.

<sup>60</sup> Jacobson, C. A., *J. Phys. Chem.*, 27, 577, 761, 1923; *ibid.*, 28, 506, 1924.

should be double that in the first. Hence, from the difference in the two titrations the total of other acids can be calculated and is usually expressed as HF: % HF = (% Total Acidity as  $\text{H}_2\text{SiF}_6$  - %  $\text{H}_2\text{SiF}_6$ )  $\times$  0.278.

Remarks.—A negative correction of 0.6%  $\text{H}_2\text{SiF}_6$  has been recommended to compensate for the consumption of NaOH by silicic acid.<sup>60</sup> Free silica, where present in significant amounts, may be estimated from the difference in the first titration conducted with and without the addition of (neutral) fluoride. A more elegant procedure for fluosilicic acid high in silica has been reported.<sup>61</sup>

A less exacting approach<sup>62</sup> is to titrate a sample of  $\text{H}_2\text{SiF}_6$  (3 g.) with NaOH to the phenolphthalein end point at room temperature; then to heat to 70 to 80°C., and titrate with NaOH to a permanent pink. The total volume of NaOH required is used to calculate the percentage of total acidity as  $\text{H}_2\text{SiF}_6$ , which may be simply taken as the percentage of  $\text{H}_2\text{SiF}_6$ .

$$\% \text{H}_2\text{SiF}_6 = \frac{(\text{milliliters of NaOH}) \times (\text{normality of NaOH}) \times 0.024015 \times 100}{\text{sample weight in grams}}$$

where the volume of NaOH is corrected for temperature.

### DETERMINATION OF RESIDUE ON IGNITION FOR FLUOSILICIC ACID

The determination of the residue on ignition for fluosilicic acid is frequently accomplished by addition of a few drops of sulfuric acid to a suitable sample (5 g.), and evaporation followed by ignition. Some workers prefer to add some hydrofluoric acid (2 ml.), as well as sulfuric acid (2 drops), to assure volatilization of silica.

### OTHER DETERMINATIONS FOR FLUOSILICIC ACID

Where of interest, the determination of iron, chloride, sulfate, and "heavy metals" in fluosilicic acid parallels the procedures given for sulfuric acid. For the determination of iron, a suitable sample is evaporated twice after the prior addition of 2 ml. of HCl, and the thiocyanate procedures given for iron in sulfuric acid are employed (p. 549). For the determination of chloride, a 5-g. sample is evaporated to dryness after the addition of 15 mg. of sodium carbonate, the residue is taken up in water, and the turbidimetric procedure for chloride in sulfuric acid applied (p. 542). For the determination of heavy metals, the general procedure given under sulfuric acid (p. 548) is appropriate.

### FLUOSULFONIC ACID

Fluosulfonic acid,  $\text{FSO}_3\text{H}$ , is offered commercially in a 96% technical grade. The product is usually manufactured to contain about 1% free sulfur trioxide; on a custom-basis, however, it can be supplied with an excess of hydrofluoric acid. The most expeditious approach to the determination of the composition of the usual product is a conductometric titration of free sulfur trioxide with water and measurement of the specific conductivity at the point where all of the free sulfur trioxide has been converted to sulfuric acid. The conductivity value is related to the composition by the use of tables. (If the product contains free hydrofluoric

<sup>61</sup> Thomsen, S. M., *Anal. Chem.*, **23**, 973, 1951.

<sup>62</sup> Kern, E. F., and Jones, T. R., *Trans. Am. Electrochem. Soc.*, **57**, 273, 1930.

acid, a known amount of 100% sulfur trioxide is added initially.) Sulfur dioxide is determined by an iodimetric titration similar to that employed for sulfuric acid (see p. 545).<sup>63</sup>

### HYDROFLUORIC ACID

Hydrofluoric acid, HF, is offered commercially as anhydrous liquid hydrogen fluoride (99.6% and 99.9% minimum) in steel cylinders, and as aqueous solutions, the usual strengths being 30, 45, 52, 60, and 70% HF. Reagent grade hydrofluoric acid, meeting American Chemical Society specifications, is available as 48 to 51% HF. The analyst should be alerted to the special hazards associated with the handling of this acid.<sup>64</sup>

The analysis of anhydrous hydrogen fluoride generally parallels that of the aqueous solution following initial solution of the sample with water-ice or frozen sodium chloride solution. As special handling techniques and precautions are involved, however, the special literature should be consulted.<sup>65</sup> Indeed, that literature is best consulted for additional details on the analysis of the anhydrous acid.

For the analysis of acid etch mixtures containing hydrofluoric acid, see p. 585.

The analysis of hydrofluoric acid has been facilitated in recent years by the availability of plastic laboratory ware, which can be substituted for the platinum, silver, or wax-lined vessels formerly employed in many operations. Hydrofluoric acid can be evaporated at temperatures as high as 200°C.<sup>66</sup> in dishes machined from polytetrafluoroethylene (Teflon).

### DETERMINATION OF HYDROFLUORIC ACID AND FLUOSILICIC ACID IN HYDROFLUORIC ACID

The total acidity of hydrofluoric acid is often determined by an alkalimetric titration in *cold* solution in the presence of potassium nitrate, which precipitates potassium fluosilicate. The resulting solution is then heated, thus hydrolyzing fluosilicate, and the additional acidity developed is titrated alkalimetrically (for relevant equations, see p. 577). From these results and the independent determination of sulfuric acid and of sulfurous acid, the actual hydrofluoric acid content is calculated. Alternatively, and especially where only a relatively small amount of fluosilicic acid is present, the total acidity is determined by the alkalimetric titration in *hot* solution, and the fluosilicic acid content is determined independently by a photometric silicomolybdate procedure.

**Titrimetric Procedure for Total Acidity in Cold Solution.**—In a platinum weighing tube, with a platinum wire loop attached to the lid (to facilitate its removal with a plastic stirring rod), establish a suitable sample (2.5 g. of 70% HF). Place 10 ml. of saturated KNO<sub>3</sub> solution, some chipped ice, 75 ml. of 1 N NaOH (from a chamber buret) and some drops of phenolphthalein indicator solution in a polypropylene beaker. Now invert the weighing tube beneath the surface of the

<sup>63</sup> Personal communication, M. R. Singer, Allied Chemical Corp.

<sup>64</sup> See Manufacturing Chemists' Association, Inc., 1825 Connecticut Avenue N.W., Washington, D. C., Chemical Safety Data Sheet SD-25, Hydrofluoric Acid, 48 pp. Have at hand a magnesium oxide-glycerin paste and, on any *suspicion* of contact with hydrofluoric acid, apply to the skin after prolonged flushing with cold water.

<sup>65</sup> Swinehart, C. F., and Flisik, H. F., Ind. Eng. Chem., Anal. Ed., 16, 419, 1944; Sherry, W. B., et al., *ibid.*, 16, 483, 1944; Cook, C. D., and Findlater, F. G., J. Soc. Chem. Ind., 66, 169, 1947; Phillips Petroleum Co., Hydrofluoric Acid Alkylation, 1946, Chapter 7, 185–266.

<sup>66</sup> Sentementes, T. J., and De Sesa, M. A., Chemist-Analyst, 44, 54, 1955.

liquid and cautiously remove the lid. Allow the acid to mix gradually. Leave the tube and lid in the solution. Complete the titration with 1 N NaOH to the first permanent pink color, while maintaining the ice temperature. Allow the buret to drain and read the volume of NaOH delivered. Note the temperature of the NaOH solution, and add a correction of 0.00032 ml. per milliliter of 1 N NaOH added for each degree Centigrade below its standardization temperature, or subtract the correction for each degree above. (Then proceed to the determination of the fluosilicic acid content by the titration procedure given below.)

% Total Acidity (cold) as HF

$$= \frac{(\text{milliliters of NaOH}) \times (\text{normality of NaOH}) \times 0.020006 \times 100}{\text{sample weight in grams}}$$

where the volume of NaOH is corrected for temperature. When the percentages of  $\text{H}_2\text{SiF}_6$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_2\text{SO}_3$  have been determined, the actual HF content may be calculated: % HF = % Total Acidity (cold) as HF - %  $\text{H}_2\text{SiF}_6 \times 0.2777$  - %  $\text{H}_2\text{SO}_4 \times 0.4080$  - %  $\text{H}_2\text{SO}_3 \times 0.4875$ .

**Titrimetric Procedure for Total Acidity in Hot Solution.**—Proceed as in the above titration in cold solution, but substituting 50 ml. of  $\text{CO}_2$ -free water for the ice and  $\text{KNO}_3$  solution. Titrate the solution at room temperature to an approximate end point. Then heat the solution to boiling and complete the titration in the hot solution with 1 N NaOH to a permanent pink color.

% Total Acidity (hot) as HF

$$= \frac{(\text{milliliters of NaOH}) \times (\text{normality of NaOH}) \times 0.02001 \times 100}{\text{sample weight in grams}}$$

where the volume of NaOH is corrected for temperature. When the percentages of  $\text{H}_2\text{SiF}_6$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_2\text{SO}_3$  have been determined, the actual HF content may be calculated: % HF = % Total Acidity (hot) as HF - %  $\text{H}_2\text{SiF}_6 \times 0.8331$  - %  $\text{H}_2\text{SO}_4 \times 0.4080$  - %  $\text{H}_2\text{SO}_3 \times 0.4875$ .

**Titrimetric Procedure for Fluosilicic Acid.**—Heat the solution remaining from the titration of the total acidity in cold solution (see above) to about  $80^\circ\text{C}$ . and titrate with 1 N NaOH to the first permanent pink color.

$$\% \text{H}_2\text{SiF}_6 = \frac{(\text{milliliters of NaOH}) \times (\text{normality of NaOH}) \times 0.03602 \times 100}{\text{sample weight in grams}}$$

where the volume of NaOH is corrected for temperature.

**Photometric Silicomolybdate Procedure for Fluosilicic Acid.**<sup>67</sup>—Place 5 ml. of 4% NaCl solution in a platinum dish, and place in a casserole containing crushed solid carbon dioxide until the solution freezes solid. Wipe the outside of the dish and weigh on a torsion balance. Return the dish to the casserole. Add a sample of the HF containing 0.0005 to 0.0050 g. of  $\text{H}_2\text{SiF}_6$  (expediently from a plastic pipet) and reweigh the (wiped) dish. Allow the dish to stand until the ice is melted. Then place on a hot water bath, and evaporate to dryness. Wash down the walls of the dish with about 15 ml. of water, thus dissolving the residue. Add 10 ml. of saturated  $\text{H}_3\text{BO}_3$  solution and heat nearly to boiling. Cool to  $38^\circ\text{C}$ .

<sup>67</sup> Procedure, courtesy, General Chem. Div., Allied Chem. Corp.; based on Cade, G. N., Ind. Eng. Chem., Anal. Ed., 17, 372, 1945.

add 2 ml. of 5 *N* H<sub>2</sub>SO<sub>4</sub> and mix. Filter through retentive filter paper into a 50-ml. volumetric flask with rinsing of the dish and filter with warm water. Cool to 26 to 30°C. and add 5.0 ml. of a freshly filtered 10% ammonium molybdate solution while swirling the flask, dilute to the mark with water, and mix. Allow to stand 10 min. Measure the absorbance of the solution against water using a blue (425 mμ) filter. Calculate the percentage of H<sub>2</sub>SiF<sub>6</sub> from a standard curve prepared by carrying known amounts of Na<sub>2</sub>SiO<sub>3</sub> through the procedure, starting with the establishment of a volume of 15 ml. and the addition of 10 ml. of H<sub>3</sub>BO<sub>3</sub>.

**Remarks.**—A reagent blank correction may be secured by conducting the procedure omitting the addition of the HF sample and the cooling, heating, and filtration steps. Where required accuracy warrants, a more satisfactory blank may be established by carrying two different, known amounts of HF, low in H<sub>2</sub>SiF<sub>6</sub> through the procedure, and extrapolating to a nil amount of HF. Phosphate interferes to a limited extent and, where present, a further sample of the HF may be evaporated *without* the addition of NaCl and the procedure then applied; the phosphate found, expressed as % H<sub>2</sub>SiF<sub>6</sub>, may be applied as a correction to the result in the determination of % H<sub>2</sub>SiF<sub>6</sub>. A modified procedure requiring neither an initial evaporation nor neutralization of HF has been reported.<sup>68</sup>

A molybdenum blue photometric procedure is also serviceable.<sup>69</sup> Where large amounts of silica are encountered in process samples, a gravimetric method is applicable based on the precipitation of the 8-hydroxyquinolinium molybdsilicate moiety.

### DETERMINATION OF SULFURIC ACID IN HYDROFLUORIC ACID

Sulfuric acid (i.e., nonvolatile acidity) is determined in hydrofluoric acid following the procedure for this acid in fluoboric acid (see p. 575).

### DETERMINATION OF SULFUR DIOXIDE (SULFUROUS ACID) IN HYDROFLUORIC ACID

Sulfur dioxide (or sulfurous acid) may be determined in hydrofluoric acid by a conventional iodimetric titration. The sample is best weighed into a polyethylene beaker containing water.

**Procedure.**—Weigh a polyethylene beaker containing a polyethylene stirring rod and 150 ml. of ice-cold water on a torsion balance. Add about 30 g. of HF, and reweigh to establish the sample weight. At once add starch indicator and titrate with 0.1 *N* iodine to a permanent blue. To establish a blank, titrate similarly 150 ml. of the ice-cold water.

$$\% \text{ SO}_2 = \frac{(V - v) \times (\text{normality of iodine}) \times 0.03203 \times 100}{\text{sample weight in grams}}$$

where *V* and *v* are the milliliters of iodine consumed by the sample and blank respectively. The factor for % H<sub>2</sub>SO<sub>3</sub> is 0.04104.

<sup>68</sup> Jewsbury, A., *Analyst*, 75, 256, 1950.

<sup>69</sup> Brabson, J. A., Mattraw, H. C., Maxwell, G. E., Darrow, A., and Needham, M. F., *Anal. Chem.*, 20, 504, 1948.

### DETERMINATION OF RESIDUE ON IGNITION FOR HYDROFLUORIC ACID

In hydrofluoric acid, the residue on ignition is determined by evaporation of a suitable sample of the acid (15 to 20 g.), and gentle ignition of the residue.

### DETERMINATION OF IRON IN HYDROFLUORIC ACID

The determination of iron in hydrofluoric acid parallels the thiocyanate procedures for iron in sulfuric acid (see p. 549), following the complete removal of hydrofluoric acid by a double evaporation. A suitable sample of the acid is weighed into a platinum dish and evaporated on a hot plate. The residue is dissolved, with swirling, in 2 ml. of sulfuric acid and 5 ml. of hydrochloric acid, and evaporated to dryness. The same amounts of the two acids are again added and the solution is just taken to sulfur trioxide fumes. The residual solution is then transferred to a 100-ml. volumetric flask (or Nessler tube) with water rinses and the thiocyanate procedures given for sulfuric acid are thereupon followed (p. 519).

### DETERMINATION OF "HEAVY METALS" IN HYDROFLUORIC ACID

The determination of "heavy metals" in hydrofluoric acid may be effected by the general procedure given for sulfuric acid (see page 548) with sodium carbonate added in the initial evaporation.

### WATER CONTENT OF HYDROFLUORIC ACID

The Karl Fischer titration is directly applicable to the determination of hydrous hydrofluoric acid at least in the 50% strength region, the sample (0.3 g.) being added directly to 25 ml. of absolute methanol.<sup>69a</sup> This titration can also be applied to the determination of the water content in the substantially anhydrous region above about 90% HF employing a pyridine or pyridine-methanol medium. For this high strength region, a concentration method is also useful. A weighed sample in a special boiler fabricated of platinum is placed in a steam bath and is evaporated until the boiling point reaches exactly 90°F. The residue, which corresponds to a 90% HF-10% H<sub>2</sub>O composition, is weighed. The water content of the original sample may then be calculated, applying a correction for any nonvolatile acid present in significant amounts.<sup>69b</sup>

### OTHER IMPURITIES IN HYDROFLUORIC ACID

Where of interest, other impurities in hydrofluoric acid may be determined by the procedures given for other mineral acids. Trace chloride may be determined turbidimetrically, phosphate by a photometric molybdenum blue procedure after initial evaporation, and arsenic by the general Gutzeit procedure after an initial evaporation with added sulfuric acid. Copper, lead, and nickel may be determined by photometric methods. The spectrographic examination of trace impurities in hydrofluoric acid parallels that given for nitric acid (see p. 565). For the analysis of reagent grade hydrofluoric acid, relevant monographs should be consulted (see footnote 27, p. 552).

<sup>69a</sup> Mitchell, J., and Smith, D. M., *Aquameyry*, Interscience, New York, 1948, p. 243.

<sup>69b</sup> Procedure, General Chem. Div., Allied Chem. Corp.

## PHOSPHORIC ACID

Phosphoric acid (i.e., ortho-phosphoric acid),  $\text{H}_3\text{PO}_4$ , is commonly offered in the technical grade in strengths of 50, 75, and 85%  $\text{H}_3\text{PO}_4$  and in a food grade as 50% and 75%. Products containing more phosphorus pentoxide than present in 100% phosphoric acid are receiving increasing commercialization and the 105%  $\text{H}_3\text{PO}_4$  strength (i.e., 76% Total  $\text{P}_2\text{O}_5$ ) is well-established. A reagent grade, meeting American Chemical Society specifications, has a strength of 85–87%  $\text{H}_3\text{PO}_4$ . Specific gravity-composition data for 30–110% phosphoric acid are given in the table on page 622. For information on the analysis of alkaline phosphates, complex phosphates and lower oxy-acids of phosphorus, see Vol. I, Chapter 35.

## PHOSPHORIC ACID CONTENT

Since phosphoric acid is a nonvolatile acid, no special precautions are needed in the establishment of its phosphoric acid content.

## PHOSPHORIC ACID CONTENT BY SPECIFIC GRAVITY

Since the specific gravity of aqueous solutions of phosphoric acid increases regularly and shows considerable spread over the entire range of concentrations encountered in commercial products, hydrometer measurements are favored for product control.

*Procedure for Specific Gravity by Hydrometer.*—With a hydrometer graduated to read specific gravity at 15.5°C. (or 60°F.) compared to water at 15.5°C. (or 60°F.), take the hydrometer reading of the  $\text{H}_3\text{PO}_4$  sample at room temperature (21–29°C.) taking the usual precautions (see page 534). Also record the temperature. (If the hydrometer and associated thermometer have been calibrated, correct the values accordingly.) Calculate the specific gravity at 25°C. compared to water at 15.5°C. from the allowances for temperature given at the end of the table on page 622 and from that table the %  $\text{H}_3\text{PO}_4$ . For some purposes the result is expressed as %  $\text{P}_2\text{O}_5 = \text{H}_3\text{PO}_4 \times 0.72426$ .

*Example.*—For a  $\text{H}_3\text{PO}_4$  sample a hydrometer value of 1.568 was found at 28.1°C. (as corrected for the hydrometer and thermometer calibration data). From the table (page 622), the approximate strength is 75%  $\text{H}_3\text{PO}_4$ ; hence, the allowance per degree, according to the table, is 0.00075. Hence, specific gravity 25°/15.5°C. =  $1.568 + (28.1 - 25.0) \times 0.00075 = 1.570$ . Therefore by interpolation in the table, the %  $\text{H}_3\text{PO}_4$  is found to be 74.60%. The %  $\text{P}_2\text{O}_5 = 74.60 \times 0.72426 = 54.03\%$ .

## PHOSPHORIC ACID CONTENT BY TITRATION

Only the first two hydrogens of phosphoric acid are sufficiently strong to permit their simple, direct titration with a strong base in an aqueous medium. However, the *visual* titration of either of the hydrogens requires special considerations in order to secure satisfactory results; hence a potentiometric titration is often preferred using a pH-meter with a calomel-glass electrode pair. Where other *strong* acids are present, the difference in the results of the titration to the pH values represented by the first and second hydrogens corresponds to phosphoric acid only (see Vol. I, pages 816–818 for further details). Where high precision and selectivity is sought, as in referee analysis, either a magnesium pyrophosphate gravimetric method (Vol. I, page 812) or a phosphomolybdate titrimetric method (Vol. I, page 814) is recommended.



## DETERMINATION OF SULFATE IN PHOSPHORIC ACID

Where encountered in sufficient amounts, sulfate may be determined gravimetrically as barium sulfate by the conventional procedure (Vol. I), following initial boiling of the diluted phosphoric acid sample with hydrochloric acid (Vol. I, page 862). Trace amounts of sulfate may be determined by a sulfide evolution method (see Vol. I, page 862, and this volume, page 567).

## DETERMINATION OF "HEAVY METALS" IN PHOSPHORIC ACID

Heavy metals are determined in phosphoric acid essentially by the procedure of the *National Formulary*. For further information on the "heavy metals" concept, see page 548.

**Heavy Metals Procedure.**—Place a suitable sample of  $\text{H}_3\text{PO}_4$  (1 g. of 85%  $\text{H}_3\text{PO}_4$ ) in a 50-ml. Nessler tube, add about 10 ml. of water and 5.5 ml. of 1% NaOH solution. Stir and dilute to about 25 ml. with water. Now add 10 ml. of saturated  $\text{H}_2\text{S}$  water, stir gently, and dilute to 50 ml. with water. Compare the color developed with that of standards containing 0 to 0.05 mg. of lead (as the nitrate salt) and 2 ml. of 1 N acetic acid (omitting the NaOH addition). As a photometric procedure compare the unknowns and standards against water using a blue filter. Express the result as % Heavy Metals as Lead = (mg. of Pb in standard matching the sample preparation)  $\times 0.1 \div$  (sample weight in g.).

## DETERMINATION OF OTHER IMPURITIES IN PHOSPHORIC ACID

Arsenic is determined in phosphoric acid, especially for the purity grades, by the modified Gutzeit method given in Vol. I, page 757, with an increase in sample size, if appropriate. Fluoride is determined by a Williard-Winter distillation with perchloric acid added, followed either by a precipitation titration or a photometric determination (see Vol. I, Chapter 18 and page 842, also the remark in this volume on page 562). Iron may be determined photometrically by an *o*-phenanthroline procedure (see Vol. I, page 553); however, the reduction of iron(III) is preferably effected with sodium dithionite in a citrate medium at pH 5–6.<sup>70</sup> Aluminum in substantial amounts in crude phosphoric acid may be determined gravimetrically by an 8-quinolinol procedure or small amounts by a photometric aluminon procedure (see Vol. I, page 856). Calcium in crude phosphoric acid may be determined by classical methods (Vol. I, Chapter 11) or probably best by an ethylenediaminetetraacetate titration at pH 12–12.5 with murexide, Calcon, or other suitable metal indicator (see Vol. I, page 265), following removal of the bulk of the phosphate by precipitation with iron(III) and filtration,<sup>71</sup> by solvent extraction of the phosphomolybdate moiety<sup>72</sup> (see Vol. I, page 858), or by anion exchange.<sup>73</sup> For the analysis of pharmaceutical grade and reagent grade phosphoric acid, relevant monographs should be consulted (*National Formulary* and works cited in footnote 27 on page 552).

<sup>70</sup> Grat-Cabanac, M., *Anal. Chim. Acta*, 17, 588, 1957.

<sup>71</sup> Łasiewicz, K., Byczyńska, B., and Zawadzka, H., *Chem. Anal. (Warsaw)*, 3, 1041, 1948; *Anal. Abstr.*, 7, 1282, 1960.

<sup>72</sup> Collier, R. E., *Chemist-Analyst*, 43, 41, 1954.

<sup>73</sup> Mason, A. C., *Analyst*, 77, 529, 1952.

## ACID MIXTURES FOR ETCHING SEMICONDUCTORS

Mixtures of common acids have long received special and varied application; the analytical problems thus introduced have not received prominence, with the exception of those encountered with sulfuric acid-nitric acid mixtures (see page 552). The evolution of semiconductors has introduced a demand for mixtures of high purity acids for the chemical etching of these devices. At one time these acid etchants were mixed by the consuming industry; subsequently they have become items of commerce and, therefore, interest has developed in the control of their delivered composition. Holmes has discussed at length the composition and use of many of the semiconductor acid etchants.<sup>73a</sup>

The principal etchants of commerce contain various amounts of reagent grade hydrofluoric acid and nitric acid with or without acetic acid. Some compositions contain small amounts of additives, notably free bromine or iodine, and further substances, which favorably influence the etching process, may be added by the consumer. Although the control of these mixed acids is still a subject of close study, their importance prompts a brief mention of some known analytical approaches.

A major difficulty in the analysis of these acid mixtures is their rapid attack of glass, metal, and diverse materials. In practice, this consideration rules out many instrumental methods, including simple physical measurements, unless prior treatments are undertaken.

It may be noted that samples of the etchant are expeditiously weighed in commercially available polyethylene vials and transferred by the use of polyethylene pipets. Since, in the manufacture of these mixtures, stratification may occur if the agitation is insufficient, this possibility should be recognized in establishing a representative sample.

If free halogen is present in the etchant, it may be extracted initially with a halocarbon and be determined separately. Where acetic acid is present in the etchant, the organic phase should be back-washed with water to avoid losses of this acid and of nitric acid.

The nitric acid-hydrofluoric acid mixture has been resolved by titrating a sample, well diluted with water, with standard caustic to the phenolphthalein end point. The result corresponds to the total acidity. Then sodium chloride is added to the resulting solution to saturation. The solution is heated to 70° to 80°C. and acid and base are added to make the solution just alkaline to phenolphthalein. The solution is then titrated with an aluminum chloride solution to the methyl red end point. The result of the second titration corresponds to hydrofluoric acid; the nitric acid content is found by difference.<sup>73b</sup>

For the analysis of the hydrofluoric-nitric-acetic acid mixture, one group has suggested an approach that involves both acid-base titrimetry and spectrophotometry. After 50-fold dilution of one sample of the etchant with water, nitric acid is determined via its absorption in the ultraviolet at 300 m $\mu$  with water serving as the reference. The dilution of the sample reduces the rate of corrosion to a point that conventional quartz cells may be employed. Then two identical samples of the etchant are weighed; one is dissolved in water and the other in a similar volume of methanol.

<sup>73a</sup> Holmes, P. J., ed., *The Electrochemistry of Semiconductors*, Academic Press, London, 1962.

<sup>73b</sup> Based on a suggested procedure of General Electric Co.; essentially after Long, S. A., *Anal. Chem.*, 26, 1988, 1954.

The first solution is titrated with standard caustic to the phenolphthalein end point, thus providing a value for the total acidity. The methanolic solution is refluxed for 30 minutes, thus esterifying the acetic acid. The remaining nitric and hydrofluoric acids are titrated with standard caustic under ice-cold conditions (to prevent saponification of the methyl acetate). Since the calculations depend on differences, it is best to run all titrations in duplicate.<sup>73c</sup> A further approach to the resolution of a hydrofluoric-nitric-acetic acid mixture involves both acid-base and complexometric titrimetry. Initially after dilution of the sample with water and neutralization to about pH 7, fluoride is removed by the addition of a known, excess amount of calcium chloride. The mixture is diluted to known volume and the calcium fluoride precipitate is allowed to settle. The excess of calcium ion in one portion of the clear supernatant liquid is titrated with ethylenediaminetetraacetate at a suitable pH and employing an appropriate metal indicator. A second portion of the supernatant liquid is passed through a column of a strongly acidic ion exchange resin in the hydrogen form, thus exchanging calcium for hydrogen ion. The effluent is then titrated with standard caustic potentiometrically (glass-calomel electrodes). The first titration break corresponds to the moles of nitric acid originally present and twice the moles of calcium ion added *initially*. The difference between the first and second titration breaks corresponds to the moles of acetic acid present.<sup>73d</sup> For internal plant control it may be expedient to express the results in terms of the molarity of each acid in the product, rather than in weight-weight per cent. Alternatively, the percentage results may be placed on a weight-volume basis. Either approach allows a sample to be established on a volume basis.

### FREE ACIDITY IN THE PRESENCE OF HYDROLYZABLE IONS

"Free" acidity is the amount of acid which would remain in a solution if the hydrolyzable ion were removed or replaced by a nonhydrolyzable ion (other than hydrogen ion). The determination of the free acidity is of practical importance, for example, in metal-descaling, ore-leaching and ore-processing solutions, in alums and acidic salt solutions, and in acidic electroplating baths. The direct titration with sodium hydroxide fails since the hydrolyzable ion consumes base and the visual end point may be obscured by the formation of a precipitate or may be poorly defined. In some cases, a precipitant for the hydrolyzable ion may be added, for example potassium fluoride for aluminum (in alums),<sup>74</sup> and iron(III),<sup>74,75</sup> and sodium dihydrogen phosphate for iron(III).<sup>76</sup> Alternatively an agent forming soluble complexes may be added, for example, oxalate for various ions,<sup>77</sup> copper(II)<sup>78</sup> and aluminum,<sup>79</sup> and citrate for iron(III).<sup>80</sup>

<sup>73c</sup> Jones, J. W., and Dendy, J. M., paper, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1961; procedure of Texas Instruments, Inc.

<sup>73d</sup> Morgenthaler, L. P., unpublished work; procedure of Western Electric Co., Inc., Engineering Research Center, Princeton, New Jersey.

<sup>74</sup> Eder, T., *Z. anal. Chem.*, **119**, 399, 1940; Scott, W. W., *J. Ind. Eng. Chem.*, **7**, 1059, 1915; Craig, T. J., *J. Soc. Chem. Ind.*, **30**, 184, 1911.

<sup>75</sup> Kolthoff, I. M., and Stenger, V. A., *Volumetric Analysis*, Interscience Publishers, Inc., New York, Vol. II, 1947, p. 111.

<sup>76</sup> Ahlum, C. C., *Analyst*, **31**, 168, 1906; *J. Chem. Soc.*, **89**, 470, 1906.

<sup>77</sup> Booman, G. L., et al., *Anal. Chem.*, **30**, 284, 1958.

<sup>78</sup> Verma, M. R., Bhuchar, V. B., Mathur, S. K., and Sharma, S. S., *Chemist-Analyst*, **48**, 1959.

<sup>79</sup> Hahn, F. L., and Hartleb, E., *Z. anal. Chem.*, **71**, 225, 1927.

<sup>80</sup> Bishop, J. A., and Summ, S., *Chemist-Analyst*, **43**, 96, 1954.

A further approach to the establishment of free acidity involves the determination of a measure of the "total" acidity and, independently, of the concentration of the hydrolyzable cation in the sample solution, which may be expressed as "bound" acidity, and calculation of the "free" acidity by a difference method. For example, an aliquot of the acidic sample solution may be passed through a cation exchange column in the hydrogen form and the effluent titrated alkalimetrically. The hydrolyzable ion is then determined in a second sample aliquot by an appropriate method. A second variation involves addition of an excess of a strong chelating agent, which complexes with all of the hydrolyzable cation, and then an alkalimetric titration. The concentration of the hydrolyzable cation in the sample solution is determined in a further aliquot by either a redox or chelometric titration. The free acidity corresponds to the difference of the two results, suitably expressed.

**Procedure for Free Acidity in Presence of Iron(III) Salts.**—Saturate the acidic sample solution with sodium or potassium citrate. Add phenolphthalein and titrate with  $\text{CO}_2$ -free standard NaOH solution. As the end point is approached, add further citrate and stir well to assure saturation of the solution. The free acidity is given by the ml. of NaOH added, since the secondary citrate ion,  $\text{H}_2\text{Cit}^-$ , is completely neutralized at the phenolphthalein end point.<sup>80</sup>

**Remarks.**—The procedure is especially applicable to hydrochloric acid liquors used in descaling iron. The iron must be in the trivalent state for the complexation to be fully effective. Where preferred, iron(III) may be precipitated with  $\text{NaH}_2\text{PO}_4$  and the mixture titrated to the methyl orange end point; or this metal may be precipitated with potassium fluoride solution (neutralized to the faint pink color of phenolphthalein), the mixture diluted to known volume, and an aliquot of the clear supernatant liquid titrated to the phenolphthalein end point.

**Procedure for Free Acidity in Presence of Bismuth, Iron(III), or Chromium(III) Salts.**—To a measured volume of the sample solution, add a volume of a water solution of disodium ethylenediaminetetraacetate sufficient to complex all hydrolyzable cations present and about 1% in excess of the stoichiometric amount required. If a precipitate appears, stir until solution is complete. (A concentrated solution of the chelating agent is preferred, especially where a high concentration of hydrolyzable cations is present, in order to reduce the dilution and thereby the formation of hydroxo complexes that react only slowly with the complexing agent.) Where chromium(III) is present, boil the solution 3 to 5 minutes to effect full complexation, and cool.

Titrate the resulting solution with a standard NaOH solution (0.1 or 1 N) potentiometrically (glass-calomel or quinhydrone-calomel electrode pair) or in the case of a colorless solution (e.g., bismuth salt solutions) to a visual end point with methyl red or methyl orange. Record the volume of base required.

Now determine the molar concentration of the hydrolyzable metal ion in the sample solution. For chromium(III), oxidize to chromium(VI) and apply a redox titration (see Vol. I, pp. 354–6, 361–2). For bismuth, employ a direct ethylenediaminetetraacetate titration with thiourea as the indicator (see Vol. I, pp. 199–200) or better, xylenol orange (titrating at pH 1 to 3 to a red to yellow end point). For iron(III), use either a redox titration (see Vol. I, pp. 538–52) or a direct ethylenediaminetetraacetate titration with sulfosalicylic acid as the indicator (titrating at pH 1.8 to 3.0 in warm solution to a red-violet to yellow end point).

The free acidity of the sample solution, expressed as % weight-by-volume, is given by

$$\% \text{ Free Acidity (w/v)} = \left( \frac{N_b \times V_b}{a} - 2[Me^{n+}] \right) \times \frac{E}{10}$$

where  $N_b$  and  $V_b$  are the normality and volume of the NaOH solution used in the alkalimetric titration of  $a$  milliliters of the sample solution,  $E$  is the equivalent weight of the relevant acid in the sample solution, and  $[Me^{n+}]$  is the molar concentration of the hydrolyzable metal ion in the sample solution. It is noteworthy that in this equation the factor 2 is required as 2 moles of hydrogen ion are liberated in the complexation of 1 mole of metal ion with ethylenediaminetetraacetate.<sup>80a</sup>

### FORMIC ACID

Formic acid,  $\text{HCO}_2\text{H}$ , boiling point  $100.5^\circ\text{C}$ ., is available in a technical grade in 85% and 90% strengths and a reagent grade, meeting American Chemical Society specifications, containing 88%  $\text{HCO}_2\text{H}$  minimum. A purified grade of 98% minimum  $\text{HCO}_2\text{H}$  content is available in small package sizes. Formerly a pharmaceutical grade containing 24–26%  $\text{HCO}_2\text{H}$  was also employed (see *National Formulary IX*).

#### DETERMINATION OF FORMIC ACID CONTENT<sup>81</sup>

If formic acid is present alone (with water) or other acids are present in negligible amounts, a conventional alkalimetric titration of the total acidity serves for the establishment of the formic acid content. Where other acids are present (that do not react readily with permanganate), a redox titration is preferable. Usually permanganate is added to an alkaline solution (thus avoiding the volatilization of formic acid in acidic solution and its slow rate of oxidation to carbon dioxide and water in the cold), the solution is acidified, an excess of oxalate is added, and a back-titration performed.

**Alkalimetric Titration Procedure.**—Since formic acid is a volatile acid, employ one of the special techniques in the establishment of the sample (see pages 535 through 539). Transfer the sample (1.9–2.3 g. of 90%  $\text{HCO}_2\text{H}$ ) to 200 ml. of  $\text{CO}_2$ -free water in a stoppered flask or bottle. Titrate with 0.5  $N$  NaOH from a chamber buret (see footnote page 536) to the phenolphthalein end point. Allow the buret to drain and read the volume of NaOH delivered. Note the temperature of the NaOH solution and add a correction of 0.00030 ml. per ml. of 0.5  $N$  NaOH added for each degree Centigrade below its standardization temperature; or subtract the correction for each degree above. The % Total Acidity as  $\text{HCO}_2\text{H}$  = %  $\text{HCO}_2\text{H}$  (if no other acids present) = (ml. of NaOH, corrected for temperature)  $\times$  (normality of NaOH)  $\times$  0.046026  $\times$  100  $\div$  (sample weight in g.).

**Redox Titration Procedure.**—Since formic acid is a volatile acid, employ one of the special techniques in the establishment of the sample (see pages 535 through 539). Transfer the sample (2 g. of 90%  $\text{HCO}_2\text{H}$ ) to a 500-ml. volumetric flask containing about 200 ml. of water. Dilute to mark with water. Transfer a 50 ml. aliquot to a conical flask and make alkaline with  $\text{Na}_2\text{CO}_3$ . Warm the solution and add a known, excess amount of 0.1  $N$  (i.e., 0.02  $M$ )  $\text{KMnO}_4$  from a 100-ml. buret. Add 0.1  $N$  (i.e., 0.05  $M$ ) oxalic acid in excess of that needed to dissolve the

<sup>80a</sup> Polyak, E. A., Zhur. Anal. Khim., 17, 355, 1962.

<sup>81</sup> For additional methods for the determination of formic acid, see J. B. McNair, *Analysis of Fermentation Acids*, Westernlore Press, Los Angeles, 1947, chapters 2 and 3.

MnO<sub>2</sub> precipitate and also 10 ml. of 6 N H<sub>2</sub>SO<sub>4</sub>. Titrate the excess of oxalic acid with the 0.1 N KMnO<sub>4</sub>. Note the *total* volumes of oxalic acid and KMnO<sub>4</sub> delivered. In a separate titration establish the equivalency of these two solutions, expressed as  $F = \text{ml. of KMnO}_4 \text{ solution equivalent to exactly 1 ml. of oxalic acid solution}$ . Then the % HCO<sub>2</sub>H =  $(\text{ml. of KMnO}_4 - \text{ml. of oxalic acid} \times F) \times (\text{normality of the KMnO}_4) \times 0.023013 \times 100 \div (\text{sample weight in g. represented by the solution aliquot taken})$ .

Remarks.—Some workers prefer a redox titration method based on addition of an excess KMnO<sub>4</sub> to the alkaline sample aliquot, heating to 70°C., addition of a sufficient amount of KI solution, and back-titration with standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution.

### DETERMINATION OF IMPURITIES IN FORMIC ACID

Small amounts of sulfate in formic acid are determined by the turbidimetric or photometric barium sulfate procedures given for sulfate in nitric acid (see page 560). Chloride is determined turbidimetrically as silver chloride. An appropriate sample of the acid (10 ml. of 90% HCO<sub>2</sub>H) is added to 50 ml. of chloride-free water and 3 drops of concentrated nitric acid added. The procedure thereafter follows that given for chloride in sulfuric acid (see page 542), except that the standards are prepared with 3 drops of nitric acid and with the sulfuric acid addition omitted (and at the level of accuracy here required omitting the addition of chloride-free formic acid). For the determination of residue on evaporation (i.e., total solids) a suitable sample is evaporated to dryness on a steam bath, dried at 105°C. and weighed. The residue is then dissolved in a little hydrochloric acid and the solution diluted to volume; aliquots of this solution can then be used for the photometric determination of lead (see page 548) and of iron (see page 549). For the analysis of reagent grade formic acid, the relevant monographs should be consulted (see footnote 27 page 552.)

### ACETIC ACID

Acetic acid, CH<sub>3</sub>CO<sub>2</sub>H or HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, is offered in the technical grade in various strengths ranging from 28% through 56% (redistilled) to the glacial acid (98% minimum). In the pharmaceutical grade, the *U. S. Pharmacopeia* describes a 36–37% strength and a glacial acid (99.4% minimum). Reagent grade (glacial) acetic acid, meeting American Chemical Society specifications, contains 99.7% HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> minimum and is also available “conforming to dichromate test.” Glacial acetic acid melts in the region 13.3 to 16.6°C., corresponding to 98% and 100% strength, respectively. Specific gravity-composition data for acetic acid appears on page 621.<sup>82</sup>

### DETERMINATION OF ACETIC ACID CONTENT OF ACETIC ACID

The measurement of the specific gravity via a hydrometer is not extremely useful for the establishment of small differences in the strength of acetic acid solutions since the variation in specific gravity is not large and a maximum exists at

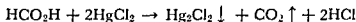
<sup>82</sup> For the analysis of vinegar, see Official Methods of Analysis, Assoc. of Official Agricultural Chemists, 9th ed., 1960, pages 413–416. (The “grain” strength of vinegar or acetic acid is ten times its acetic acid content in % wt./vol. at 20°C.; a 40 grain vinegar is 4% wt./vol. at 20°C.)

77–80% acetic acid (see table, page 621). Acetic acid is usually determined by an alkalimetric titration. Since acetic acid is a weak acid, phenolphthalein is used as the indicator and water freshly freed of carbon dioxide by boiling should be used in dilutions. The result should be corrected for the content of any other acidic materials present to obtain the "true" acetic acid content.

**Procedure for Total Acidity of Acetic Acid.**—By the use of a weighing bottle introduce a sample of 5 to 6 g. of glacial acetic acid (or its equivalent of a weaker solution) underneath the surface of 200 ml. of  $\text{CO}_2$ -free water and 75 ml. of 1 *N* NaOH (from a chamber buret, see footnote page 536) contained in a casserole. Complete the titration with 1 *N* NaOH to the phenolphthalein end point (faint permanent pink). Note the temperature of the NaOH solution and add a correction of 0.00032 ml. per ml. of 1 *N* NaOH added for each degree Centigrade below its standardization temperature; or subtract the correction for each degree above. The % Total Acidity as  $\text{HC}_2\text{H}_3\text{O}_2 = (\text{ml. of NaOH, corrected for temperature}) \times (\text{normality of NaOH}) \times 0.060053 \times 100 \div (\text{sample weight in g.})$ . If the sample contains a significant amount of other acids, a correction may be applied following their separate determination. For example, %  $\text{HC}_2\text{H}_3\text{O}_2 = \% \text{ Total Acidity as } \text{HC}_2\text{H}_3\text{O}_2 - (\% \text{ HCO}_2\text{H} \times 1.305) - (\% \text{ HCl} \times 1.647) - (\% \text{ H}_2\text{SO}_4 \times 1.225) - (\% \text{ H}_2\text{SO}_3 \times 1.463)$ .

#### DETERMINATION OF FORMIC ACID IN ACETIC ACID

The determination of formic acid in acetic acid is usually based on the reduction of mercury(II) to insoluble mercury(I) chloride, which is filtered, dried, and weighed.



**Procedure.**—Transfer a 5-g. sample of glacial acetic acid (or its equivalent of a more dilute solution) with 5 g. of sodium acetate, 40 ml. of a 5%  $\text{HgCl}_2$  solution, and 30 ml. of water to a conical flask with standard taper neck. Attach a reflux condenser and heat in a boiling water or steam bath for 2 hours. Filter the precipitate of  $\text{Hg}_2\text{Cl}_2$ , dry at  $105^\circ\text{C}$ . in an oven, and weigh. %  $\text{HCO}_2\text{H} = (\text{weight of } \text{Hg}_2\text{Cl}_2 \text{ in g.}) \times 0.0975 \times 100 \div (\text{sample weight in g.})$ .

**Remarks.**—For the routine analysis of many samples an integrated reagent may be prepared, namely, 30 g. of  $\text{HgCl}_2$  and 65 g. of sodium acetate in 1000 ml. of water; 75 ml. of this solution is used in the procedure and no water is added. For high purity acetic acid, limit tests for formic acid (and other reducing substances) are often employed based on a reaction with permanganate or dichromate ion.

The further addition of 2.5 ml. of a 2% hydroxylamine hydrochloride solution to the flask has been recommended.<sup>83</sup> This catalyzes the reduction, allows heating at  $50$ – $60^\circ\text{C}$ . for one hour, and tends to obviate any reducing action of sulfurous acid present.

Lead tetraacetate procedures have also been suggested for the determination of formic acid with the advantage that formaldehyde does not interfere.<sup>84</sup>

<sup>83</sup> Germuth, F. G., *Chemist-Analyst*, 17, No. 1, 1928.

<sup>84</sup> Perlin, A. S., *Anal. Chem.*, 26, 1053, 1954.

DETERMINATION OF SULFUROUS ACID (SULFUR DIOXIDE)  
IN ACETIC ACID

The method of determining sulfurous acid in acetic acid is based on an iodimetric titration.

**Procedure.**—To 200 ml. of water add some starch indicator and just sufficient 0.01 *N* iodine to attain a faint blue color. Now add 100 ml. of the glacial acetic acid (or an equivalent amount of a more dilute solution). Titrate with 0.01 *N* iodine to a permanent faint blue color. Record the ml. of iodine required (*after* the addition of the sample). %  $\text{H}_2\text{SO}_3$  = (ml. of iodine)  $\times$  (normality of iodine)  $\times 0.04104 \times 100 \div$  (sample weight in g.). For %  $\text{SO}_2$ , the factor is 0.03203.

## DETERMINATION OF OTHER ACIDS IN ACETIC ACID

Where present, other acids in acetic acid may be determined by conventional methods. Hydrochloric acid in small amounts may be determined turbidimetrically (page 542) or in large amounts by a Volhard titration (Vol. I, page 329) or gravimetrically as silver chloride. Small amounts of sulfuric acid may be determined turbidimetrically as barium sulfate, best after adding a small amount of sodium carbonate, evaporating to dryness, dissolving in nitric acid, and then proceeding as given for sulfate in nitric acid (page 560). Trace sulfate may be determined by a sulfide evolution method (see page 567). (Acid etch mixtures containing acetic acid are briefly considered on page 585.)

## DETERMINATION OF OTHER IMPURITIES IN ACETIC ACID

The % residue on evaporation is determined routinely via the evaporation of 100 ml. of glacial acid (or an equivalent of a more dilute solution) in a weighed porcelain or platinum dish. Often the residue is used for the determination of metals of interest, including iron by the photometric thiocyanate procedure (page 549), and for the spectrographic examination of trace impurities (see page 565). "Heavy metals" may also be determined in this residue (page 548); alternatively, the more general evaporation step for this determination may be employed as given on page 548. Where of interest small amounts of water may be determined by a spectrophotometric determination or titration based on the addition of acetic anhydride<sup>85</sup> or by the Karl Fischer method.<sup>86, 87</sup> Further elegant approaches to the determination of water are temperature rise and thermometric titration methods based on the addition of a standard acetic anhydride.<sup>87</sup>

## ACETIC ANHYDRIDE

Acetic anhydride,  $(\text{CH}_3\text{CO})_2\text{O}$ , is available in the technical grade in various strengths (in acetic acid) ranging from 75–95%, and in a reagent grade, meeting American Chemical Society specifications (97% minimum). Impurities in acetic anhydride are determined, after initial solution in water, by the established methods for acetic acid. The determination of the acetic acid anhydride content is usually based on the determination of unreacted acetic acid following the reaction of the anhydride with aniline or another base. An alkalimetric titration is possible, after

<sup>85</sup> Bruckenstein, S., *Anal. Chem.*, 28, 1920, 1956; *ibid.*, 31, 1757, 1959.

<sup>86</sup> Mitchell, J., Jr., and Smith, D. M., *Aquametry*, Interscience Publishers, Inc., New York, 1948, 444 pp.

<sup>87</sup> Greathouse, L. H., Janssen, H. J., and Haydel, C. H., *Anal. Chem.*, 28, 357, 1956.



solution of a sample of the anhydride in water; however, great care is required in the titration since any error is magnified in the final calculation of the acetic anhydride content. A modern approach which couples rapidity with good accuracy involved the addition of known amounts of water to the anhydride and measurement of the maximum temperature rise.

For 90–100% acetic anhydride, a spectrophotometric determination of its acetic acid content has been devised involving direct measurement of the sample in the near-infrared region at 1505  $m\mu$ ; the result may be expressed as % acetic anhydride.<sup>88</sup>

**Alkalimetric Titration Procedure.**—A suitable sample is dissolved in water and titrated directly with standard sodium hydroxide solution to the phenolphthalein end point, or an excess of sodium hydroxide or barium hydroxide is added and the excess of the strong base is titrated with standard sulfuric acid solution to the phenolphthalein end point. In either method the original sample solution must be allowed to stand for a sufficient time (or be warmed) to allow complete hydrolysis of the anhydride. The result of either titration corresponds to % Total Acidity as  $\text{HC}_2\text{H}_3\text{O}_2$ . (If any other acids are present and are separately determined, a value for the % Actual  $\text{HC}_2\text{H}_3\text{O}_2$  may then be obtained by appropriate subtraction.) The % acetic anhydride =  $5.667 \times (\% \text{ Total Acidity as } \text{HC}_2\text{H}_3\text{O}_2 - 100.0)$ . Since any error in the titration result is multiplied almost 5.7 times in the calculation of the anhydride content, it is imperative that temperature corrections and volume calibration data be used for the titrant solutions. Further, it is often feasible to dissolve a large amount of the acetic anhydride, repeat the titration several times, and average the results; other portions of the solution may be used for the determination of impurities.

**Aniline Procedure.**—Weigh into a tared, standard taper conical flask a suitable sample (2 g. of 95% acetic anhydride). Add 20 ml. of water, attach a reflux condenser, and heat almost to boiling for about 20 minutes. Cool, add some water, and titrate with  $\text{CO}_2$ -free 0.5 N NaOH from a chamber buret to the phenolphthalein end point. Allow the buret to drain and read the volume of NaOH delivered. Note the temperature of the NaOH solution and add a correction of 0.00030 ml. per ml. of 0.5 N NaOH added for each degree Centigrade below its standardization temperature; or subtract the correction for each degree above. Calculate the ml. of 0.5 N NaOH (corrected for temperature) required per g. of sample.

Introduce a suitable sample (2 g. of 95% acetic anhydride) into a glass-stoppered conical flask containing 20 ml. of freshly distilled aniline and previously weighed. After cooling, reweigh. Transfer the contents of the flask with alcohol rinses to a large conical flask and titrate with 0.5 N NaOH in the manner described for the initial titration. Calculate the ml. of 0.5 N NaOH (corrected for temperature) required per g. of sample.

From the difference in the two titration results, the % acetic anhydride can be calculated: %  $(\text{CH}_3\text{CO})_2\text{O}$  = (difference in the ml. of NaOH required in the titrations per g. of sample)  $\times$  (normality of NaOH)  $\times 0.10209 \times 100$ .

**Procedure for Temperature Rise Method.**<sup>89</sup>—A 200-ml. sample of the acetic anhydride and 4 ml. of the "balanced" catalyst (see below) are pipetted into a

<sup>88</sup> Fernandez, J. E., McPherson, R. T., Finch, G. K., and Bockman, C. D., *Anal. Chem.*, **32**, 158, 1960.

<sup>89</sup> Greathouse, L. A., Janssen, H. J., and Haydel, C. H., *Anal. Chem.*, **28**, 358, 1956; the original work should be consulted for additional details and for some variations on the technique.

Dewar flask fitted with an aluminum-foil covered stopper and carrying a 0–100°C. thermometer graduated in 0.1°. Record the temperature. Now add 25 ml. of distilled water, slowly until a sharp temperature rise starts and then quickly. Record the maximum temperature observed. The results are read from a curve prepared by carrying acetic anhydride standards through the procedure. Where the anhydride content is greater than about 40% the sample should be diluted with water-free acetic acid and a suitable aliquot taken.

Prepare the "balanced" catalyst as follows: To a 1:20 dilution of 60% reagent grade  $\text{HClO}_4$  with acetic acid, add while cooling the solution in an ice-water bath the calculated amount of acetic anhydride to react with the water present in both acids; store the catalyst in a tightly closed container in a refrigerator in the frozen state. (The catalytic efficacy is not impaired over a week's storage, although the preparation may yellow somewhat.)

### OXALIC ACID

Oxalic acid,  $\text{HO}_2\text{C}\cdot\text{CO}_2\text{H}$ , is offered commercially as the dihydrate,  $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ , in a technical grade (coarse crystal, typically 99.4%; fine crystal, typically 99.8%) and in a reagent grade, meeting American Chemical Society specifications. An aqueous solution of oxalic acid loses acid by volatilization at 100°C. and the anhydrous acid sublimates rapidly at 157°C.

### DETERMINATION OF OXALIC ACID CONTENT

The determination of the total acidity of oxalic acid serves for the establishment of its oxalic acid dihydrate content if a correction is applied for any other acids present, notably sulfuric acid. Alternatively and especially when other oxidizable acids are absent, a direct permanganate titration in hot solution is recommended.

**Alkalimetric Titration Procedure.**—Transfer a suitable sample (2.6–2.9 g. of  $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ ) to a casserole containing 150 ml. of  $\text{CO}_2$ -free water. Add phenolphthalein and titrate with 0.5 *N* NaOH from a chamber buret (see footnote page 536). Stir the solution during the titration to assure that all of the oxalic acid is dissolved. Record the volume of NaOH delivered. Note the temperature of the NaOH solution and add a correction of 0.00030 ml. per ml. of 0.5 *N* NaOH added for each degree Centigrade below its standardization temperature; or subtract the correction for each degree above. % Total Acidity as  $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$  = (ml. of NaOH, corrected for temperature)  $\times$  (normality of NaOH)  $\times 0.063033 \times 100 \div$  (sample weight in g.). For the % Total Acidity as  $\text{H}_2\text{C}_2\text{O}_4$ , the factor has the value 0.045018. Where other acids are present and are independently determined, a correction can be applied; for example, %  $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$  = % Total Acidity as  $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$  – %  $\text{H}_2\text{SO}_4 \times 1.285$ ; or %  $\text{H}_2\text{C}_2\text{O}_4$  = % Total Acidity as  $\text{H}_2\text{C}_2\text{O}_4$  – %  $\text{H}_2\text{SO}_4 \times 0.9180$ .

**Permanganate Titration Procedure.**—In a casserole dissolve a suitable sample (0.6 g. of  $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ ) in 100 ml. of freshly boiled and cooled water. Add 5 ml. of concentrated  $\text{H}_2\text{SO}_4$ . Then at 25–30°C. add about 90% of the 0.1 *N* (i.e., 0.02 *M*)  $\text{KMnO}_4$  required from a 100-ml. chamber buret over a period of 2 minutes with only gentle stirring. Allow the solution to stand until the pink color is discharged. Now heat the solution to 55–60°C. and continue the titration slowly (dropwise near the end point) to a pink color that persists for at least 30 seconds. Record the ml. of  $\text{KMnO}_4$  required. Run a blank titration to determine the amount of  $\text{KMnO}_4$  required to impart a similar pink color to the solution (about 0.04 ml. correction).

The %  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  = (ml. of  $\text{KMnO}_4$  required by sample - ml. of  $\text{KMnO}_4$  in blank titration)  $\times 0.063033 \times 100 \div$  (sample weight in g.). For %  $\text{H}_2\text{C}_2\text{O}_4$  the factor is 0.045018.

Remarks.—The above procedure, based on the work of Fowler and Bright,<sup>90</sup> is preferable to earlier procedures in which the entire titration is conducted in hot solution.

### DETERMINATION OF SULFATE IN OXALIC ACID

Often oxalic acid contains sufficient sulfate to permit a gravimetric determination as barium sulfate. Where only small amounts of sulfate are encountered, a turbidimetric barium sulfate procedure is employed that parallels that given for sulfate in nitric acid (see page 561).

**Gravimetric Procedure for Sulfate.**<sup>91</sup>—To a suitable sample (20 g. of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) in a platinum crucible add 5 ml. of 0.1 N NaOH. Evaporate on a hot plate and then ignite to a dull red heat on an asbestos board over a Bunsen burner. (The oxalic acid is partially volatilized and the remainder decomposed leaving the residue black.) Cool and add 10 ml. of 10 N HCl. Transfer to a 150-ml. beaker with small portions of water and boil for 5 minutes. Filter through coarse filter paper and wash with hot water. Neutralize the combined filtrate to phenol red by the addition of aqueous ammonia. Now add 15 ml. of 1 N HCl and dilute to a volume of about 130 ml. Boil and add 15 ml. of 10%  $\text{BaCl}_2$  solution to the boiling solution. Digest on a boiling water bath for 4 hours. Filter through a tared Gooch crucible ignited at 600–750°C. for 30 minutes. Wash with small portions of water until the washings are free of chloride ( $\text{AgCl}$  test), dry the crucible at 110°C. and finally ignite at 600°C. for 30 minutes. The %  $\text{SO}_4$  = (weight of ignited  $\text{BaSO}_4$ )  $\times 0.4116 \times 100 \div$  (sample weight in g.). For %  $\text{H}_2\text{SO}_4$  the factor is 0.4202.

### DETERMINATION OF OTHER IMPURITIES IN OXALIC ACID

The impurities determined in oxalic acid depend on its intended use and the grade. Chloride may be determined turbidimetrically, using nitric acid for the adjustment of the acidity of the sample solution and standards, after the procedure given for chloride in sulfuric acid (page 542). The residue on ignition and the water-insoluble matter (20-g. sample in 150 ml. of hot water) are determined by conventional methods. Where of interest, silica and iron may be determined after an initial evaporation and ignition similar to that used in the determination of sulfate in oxalic acid (see above). Silica may be determined by a molybdenum blue photometric procedure (see Vol. I, page 562) and iron by a thiocyanate procedure (see page 549). For applications in the nuclear industry, trace boron may be of some interest: An oxalic acid sample may be re-crystallized from (boron-free) water and an aliquot of the mother liquor, neutralized with sodium hydroxide; trimethyl borate distilled, and after saponification borate determined spectrophotometrically by a curcumin procedure.<sup>92</sup> For information on the analysis of reagent grade oxalic acid, relevant monographs should be consulted (see footnote 27 page 552).

<sup>90</sup> Fowler, R. M., and Bright, H. A., J. Research Natl. Bur. Standards, 15, 493, 1935.

<sup>91</sup> In part, after a procedure recommended by United Kingdom Atomic Energy Authority, P. G. Rept. 92(W), Analytical Methods for the Inspection of Oxalic Acid, H. M. Stationery Office, London, March 1960.

<sup>92</sup> United Kingdom Atomic Energy Authority, P. G. Rept. 92(W), Analytical Methods for the Inspection of Oxalic Acid, H. M. Stationery Office, London, March 1960.

## TARTARIC ACID

Tartaric acid,  $\text{HO}_2\text{C}(\text{CHOH})_2\text{CO}_2\text{H}$  or  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ , is offered commercially principally in the pharmaceutical (food) grade, meeting the tests and methods of the *National Formulary* (99.7%  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$  minimum, anhydrous basis). Tartaric acid and potassium sodium tartrate (i.e., Rochelle salt) are the ingredients of cream of tartar. Tartaric acid is also available in a reagent grade meeting American Chemical Society specifications. Because of frequent confusion, it is noteworthy that "ordinary" tartaric acid of commerce is the dextro-rotatory form and has the *LEVO*-configuration; hence, the product may be variously termed "*d*-tartaric acid," *dextro*-tartaric acid, or "*L*-tartaric acid."

## DETERMINATION OF TARTARIC ACID CONTENT

The determination of tartaric acid is best based on the isolation of potassium hydrogen tartrate, re-solution of this salt, and its alkalimetric titration.

**Procedure.**—Weigh an appropriate sample (6 g. of >45% assay and 12 g. of <45% assay) and add to 18 ml. of 20% HCl solution. Stir the mixture for 10 minutes and transfer with water rinses to a 200-ml. volumetric flask. Dilute to mark with water and mix. Filter through a dry filter into a beaker. Pipet exactly 100 ml. of the filtrate into a 250-ml. beaker and add 10 ml. of a  $\text{K}_2\text{CO}_3$  solution (66 g. of  $\text{K}_2\text{CO}_3$  per 100 ml.). Cover with a watch glass and boil gently for 20 minutes. ( $\text{CaCO}_3$  may precipitate at this point.) Transfer with water rinses to a 200-ml. volumetric flask, dilute to mark with water, and mix. Filter through a dry filter and evaporate exactly 100 ml. of the filtrate on a boiling water bath to a volume of about 15 ml. Add slowly to the hot solution with continual stirring 3.5 ml. of glacial acetic acid. Stir for 5 minutes further. Allow to stand about 20 minutes. Now add 100 ml. of 95% ethanol, stir for 5 minutes further, and allow to stand about 10 minutes until the precipitate has settled. (Some procedures recommend a longer standing time, even 2 hours or more.) Filter through a sintered glass funnel under suction. Wash the precipitate on the filter with 95% ethanol until free of acid (that is, 30 ml. of the washing should require the same volume of 0.2 *N* NaOH in its titration to the phenolphthalein end point as does 30 ml. of the original 95% ethanol). Now wash the precipitate into a porcelain casserole with about 200 ml. of hot water and titrate the hot solution with 0.2 *N* NaOH from a 100-ml. buret to the phenolphthalein end point. The %  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$  = (ml. of NaOH, corrected for temperature)  $\times$  (normality of NaOH)  $\times$  (0.7504)  $\times$  4  $\times$  100  $\div$  (original sample weight in g.).

**Remarks.**—It is probably best to standardize the base used against recrystallized potassium hydrogen tartrate. For tartrate-containing material of low assay, an empirical correction is often warranted: Deduct 0.3%  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$  for material containing less than 45% tartaric acid, 0.3% for 45–60%, and 0.2% for 60–70%. For higher assay material the correction is negligible.

Where crude tartrate preparations are being analyzed, the solution finally titrated may be highly colored; in such an event, a potentiometric end point is preferable. Where "bound" tartrate as well as "free" tartrate is to be determined, e.g., in baking powders, two equal sample aliquots are employed and in one an equivalent amount of NaOH is added rather than KOH.<sup>93</sup>

<sup>93</sup> For details see *Official Methods of Analysis of The Association of Official Agricultural Chemists*, 9th ed., 1960, p. 98.

Where the sample of tartaric acid contains negligible amounts of other acids, its determination may be based on an alkalimetric titration to the phenolphthalein end point (with *National Formulary* methods after drying the sample over  $P_2O_5$ ).

### DETERMINATION OF IMPURITIES IN TARTARIC ACID

The tartaric acid, usually offered, meets the tests and methods of the *National Formulary*, including loss on drying over phosphorus pentoxide, residue on ignition (sulfated ash), and limit tests for oxalate, sulfate, and heavy metals. The suggested specifications of the FAO include assay, sulfated ash loss on drying at  $105^\circ C.$ , and limit tests for arsenic, lead, copper, and oxalate.<sup>94</sup>

### CITRIC ACID

Citric acid,  $HO_2CCH_2C(OH)(CO_2H)CH_2CO_2H$  or  $H_3C_6H_5O_7$ , is offered principally in a pharmaceutical (food) grade, meeting *U. S. Pharmacopeia* tests and methods, and both in an anhydrous and monohydrate form (both 99.5% minimum  $H_3C_6H_5O_7$ , anhydrous basis). These forms are also available in a reagent grade meeting American Chemical Society specifications. The transition point of the monohydrate is  $36.6^\circ C.$ ; hence, recrystallization of citric acid from water above that temperature yields the anhydrous form.

### CITRIC ACID CONTENT

The citric acid content of either anhydrous citric acid or its monohydrate may be determined by an alkalimetric titration if other acids are present in negligible amounts. For general purposes, the more selective pentabromoacetone method is recommended. This method is based on the bromination and degradation of citric acid to pentabromoacetone, which in the case of large amounts of citric acid may be weighed; however, strict attention to details is necessary in order to secure satisfactory results.

**Alkalimetric Titration Procedure.**—Titrate a suitable sample (3 g. of 100%  $H_3C_6H_5O_7$ ) in 50 ml. of water with 0.5 N NaOH from a 100-ml. chamber buret (see footnote 3 page 536) to the phenolphthalein end point. Allow the buret to drain and record the volume of NaOH delivered. Note the temperature of the NaOH solution and add a correction of 0.00030 ml. per ml. of 0.5 N NaOH added for each degree Centigrade below its standardization temperature; or subtract for each degree above. The % Total Acidity as  $H_3C_6H_5O_7$  = %  $H_3C_6H_5O_7$  (if other acids absent) = (ml. of NaOH, corrected for temperature)  $\times$  (normality of NaOH)  $\times$   $0.06404 \times 100 \div$  (sample weight in g.) For %  $H_3C_6H_5O_7 \cdot H_2O$ , the factor is 0.07005.

**Pentabromoacetone Gravimetric Procedure.**<sup>95</sup>—Weigh a suitable sample (2.8 g. of 100%  $H_3C_6H_5O_7$ ), transfer to a 500-ml. volumetric flask, and dilute to mark with water. Pipet 50 ml. of this solution to a 250-ml. glass-stoppered flask. Add 18 ml. of 50%  $H_2SO_4$  and 10 ml. of a 40% KBr solution. Warm the solution to  $55^\circ C.$  Add slowly 40 ml. of 5%  $KMnO_4$  solution with occasional shaking. ( $MnO_2$  will precipitate at this point.) Allow to stand 10 minutes with occasional shaking. Add 50 ml. of a  $FeSO_4$  solution (250 g. of  $FeSO_4 \cdot 7H_2O$  in 700 ml. of water and

<sup>94</sup> Food and Agricultural Organization of the United Nations, Specifications for Identity and Purity of Food Additives, 3rd Rept., Joint FAO/WHO Expert Committee, 1958.

<sup>95</sup> Based partially on a procedure of Charles Pfizer & Co., Inc.; cf. Kuntz, E., *Z. anal. Chem.*, 54, 126, 1915, and R. Arch. Chem. Mikroskop., 7, 285, 1914.

the temperature and hydrometer. (Where the desired precision demands, repeat the measurement with 1 or 2 further portions of the cooled sample.) If a degree of accuracy no higher than 0.2° Baumé, Light can be tolerated, the hydrometer will usually not require calibration; otherwise, it must be calibrated at 60°F. and the correction applied to the value read.<sup>102</sup> Further, the thermometer must be calibrated for precision work, and the temperature read corrected by the calibration data. The Baumé reading must then be corrected to 60°F. by the application of the "allowance" data at the foot of page 626 and the %  $\text{NH}_3$  established by interpolation in the specific gravity-composition table for aqua ammonia given on that page. For the important region 24–27%  $\text{NH}_3$ , the table on page 623 is similarly utilized.

**Example of Calculation.**—For a given sample a value of 25.25°Bé, Light, corrected for the hydrometer calibration, was found at a (corrected) temperature of 45.0°F., °Bé, Light (at 60°F.) =  $25.25 + 0.052 \times (60.0 - 45.0) = 25.25 + 0.78 = 26.03^\circ\text{Bé}$ . The factor 0.052 is found in the "allowance" data on the foot of page 623. From the table on that page by interpolation it is found that %  $\text{NH}_3 = 29.46\%$ .

**Acidimetric Titration Procedure.**—Weigh a suitable sample (not more than 2.6 g. of 29%  $\text{NH}_3$ ) into a glass-stoppered weighing bottle. Slide the bottle, with the stopper in place, into a 500-ml. glass-stoppered conical flask containing 200 ml. of water. Add from a buret a volume of 0.5 N  $\text{H}_2\text{SO}_4$  sufficient to combine with the  $\text{NH}_3$  in the sample and about 10 ml. in excess. Stopper the flask. Now warm gently, thereby forcing the stopper from the weighing bottle and allowing the ammonia to mix with the acidic solution. Cool the solution, add some methyl red, and titrate the excess of  $\text{H}_2\text{SO}_4$  with 0.5 N NaOH. Compare the sodium hydroxide and sulfuric acid solutions in a separate titration, and let  $F$  = ml. of  $\text{H}_2\text{SO}_4$  equivalent to exactly one ml. of NaOH. %  $\text{NH}_3 = (\text{ml. of } \text{H}_2\text{SO}_4 - \text{ml. of NaOH} \times F) \times (\text{normality of } \text{H}_2\text{SO}_4) \times 0.017031 \times 100 \div (\text{sample weight in g.})$ .

**Remarks.**—Some workers prefer to add the ammonia sample via a sealed bulb which is broken by violent agitation of a heavy walled flask or bottle (see page 538 for details of this sealed bulb technique).

## DETERMINATION OF SULFATE IN AQUA AMMONIA

**Procedure.**—Transfer a suitable sample (100 g. of 29%  $\text{NH}_3$ ) to a 250-ml. beaker. Add 10 ml. of 1%  $\text{Na}_2\text{CO}_3$  solution and evaporate to a volume of about 10 ml. Add 10 ml. of saturated bromine water (to assure oxidation of all sulfur to sulfate) and evaporate just to dryness. Dissolve the residue in a little HCl and repeat the evaporation. Then proceed according to the turbidimetric procedure for sulfate in nitric acid (page 560), omitting the first sentence. Some workers prefer to conduct the turbidity measurement in 50-ml. Nessler tubes rather than test tubes.

<sup>102</sup> For the calibration, prepare methanol-water mixtures of about 25.25 and 26.00°Bé, Light (where 23–28%  $\text{NH}_3$  is to be determined), and take their hydrometer readings at exactly 60°F. Since the surface tension of water-methanol and aqua ammonia differ, a correction is necessary. Add to each reading the following correction:  $13.9 \div (\text{length in mm. of } 1^\circ\text{Bé on hydrometer stem} \times \text{diameter of the stem in mm.})$ . The hydrometer correction is then obtained by subtracting the corrected °Bé established by the hydrometer from the °Bé established pycnometrically. The correction, thus obtained, for the two solutions is averaged.

## DETERMINATION OF OTHER IMPURITIES IN AQUA AMMONIA

The residue on ignition may be determined after evaporation in a platinum dish (without addition of sulfuric acid). Iron can then be determined by fuming the resulting residue with potassium bisulfate and applying a photometric thiocyanate procedure (see page 549). The color of aqua ammonia is assessed either by a limit test (for "Grade B") employing a chromate standard (0.06 g.  $K_2Cr_2O_7$  in 100 ml. of dilute  $H_2SO_4$ ) or by the use of the APHA visual method for the color of water employing the platinum-cobalt standards for color units 1 through 15.<sup>103</sup> Organic matter is controlled by a limit test involving decolorization of permanganate. Hydrogen sulfide may be determined by the iodometric procedure given for crude ammoniacal liquor (see Vol. I, page 764). For the analysis of aqua ammonia of pharmaceutical and reagent grades, relevant monographs should be consulted (*U. S. Pharmacopeia* and works cited in footnote 27 page 552).

## SODIUM HYDROXIDE

Sodium hydroxide (caustic soda), NaOH, in the technical and commercial grades is often sold on the basis of its  $Na_2O$  content and common nominal strengths include 60, 70, 74, and 75.5%  $Na_2O$  (corresponding to 77.4, 90.3, 95.5, and 97.4% NaOH), the last strength being considered the "anhydrous" form. Also 50% and 73% NaOH solutions, often known as caustic liquors, are offered; the former melts at 53°F. and the latter at about 145°F. The *U. S. Pharmacopoeia* recognizes a product having a total alkalinity of 95% minimum expressed as NaOH and including not more than 3%  $Na_2CO_3$ . The reagent grade, meeting American Chemical Society specifications, contains 97% NaOH minimum and the low-carbonate form 98% NaOH minimum and 0.5%  $Na_2CO_3$  maximum. In addition a 50% solution (also low in carbonate) is available in the reagent grade in polyethylene containers. In the various grades, solid sodium hydroxide is offered in various physical forms including fused, stick, flake, pellet, and powder. Specific gravity-composition data for sodium hydroxide solutions are given on pages 624-625.

The analysis of potassium hydroxide is completely analogous to that for sodium hydroxide; hence, factors for the calculations of results for the potassium hydroxide analysis are given parenthetically in the procedures below.

## SAMPLING OF SODIUM HYDROXIDE

Since sodium hydroxide can absorb both carbon dioxide and water from the atmosphere, special considerations apply in its sampling. With the fused form, packed in steel drums, it should be recognized that visible segregation of impurities occurs in the lower portion of the block, known as the "cone," as distinguished from the remainder of the cake, known as the "body." Hence, the block, after removal from the drum, should be split lengthwise and material from both the cone and the body should be separately analyzed. From the separate results average values for the entire drum are established based on the estimated relative amounts of the cone and body. (Alternatively a composite sample mixed in these relative proportions may be analyzed.) For reduction to suitable size for analysis,

<sup>103</sup> Am. Public Health Assoc., Standard Methods for the Examination of Water, Sewage, and Industrial Wastes, New York, 10th Ed., 1955, pages 87-89.

the block samples are wrapped in a flannel cloth and hit with a mallet. With the flake and powdered forms, the top layer in the shipping container is removed to a depth of 3–4 inches, and the sample taken from the central area exposed. All samples should be immediately placed in tightly closed containers.

With the caustic solutions and liquors, as offered in tank cars and tank wagons, heating may be necessary to assure complete liquefaction, and a composite sample is established during the unloading or by repeated dipping at different depths in the tank itself. The sample should be stored in a tightly closed bottle (preferably of polyethylene if silica is to be determined). It is expedient to dissolve a weighed amount of the sodium hydroxide sample in water (as soon as delivered to the laboratory), to dilute to known volume, and to employ aliquots in the determination of total alkalinity, carbonate, chloride and chlorate. A further acidified sodium hydroxide sample solution may be used for the determination of trace amounts of iron, copper, and nickel.

**Preparation of Sodium Hydroxide Sample Solution.**—With any form of the caustic, assure that a thoroughly mixed (and representative) sample has been secured. Transfer about 50 g. of the NaOH sample into a weighing bottle and weigh the bottle and contents. Remove a suitable sample (35 g. of 100% NaOH) to a beaker and dissolve at once in CO<sub>2</sub>-free water. Transfer to a 500-ml. volumetric flask (preferably borosilicate glass), dilute to mark with CO<sub>2</sub>-free water, and mix. Reweigh the weighing bottle, thus determining the sample weight by difference. (For KOH, a suitable sample weight is 45 g. of 100% KOH.)

**Preparation of Sodium Hydroxide Sample Solution for Trace Metal Analysis.**—Weigh a suitable NaOH sample (35 g. of 100% NaOH), transfer to a beaker, and dilute or dissolve in about 100 ml. of water. Now pour the solution slowly and with stirring into a second beaker containing 100 ml. of 10 N HCl. Rinse the first beaker with water and add the rinsings to the contents of the second beaker. Heat the solution to boiling, cool, and transfer to a 250-ml. volumetric flask. (If the solution in HCl is incomplete, decant the clear supernatant liquid to the flask and re-treat the residue with concentrated HCl and HNO<sub>3</sub>, heat, evaporate nearly to dryness, dissolve in water, and add the solution to the flask.) Dilute the acidic solution to mark with water. Label the result "Sodium Hydroxide Sample Solution for Trace Metal Analysis."

Also prepare a reagent blank by evaporating 100 ml. of the 10 N HCl to dryness (as well as the amounts of any other acids added in the sample or residue treatment) and dilute exactly to 250 ml. with water. Label the result "Acid Reagent Blank for Trace Metal Analysis." Use portions of this sample solution and reagent blank in the determination of copper and nickel (and also of iron if this is determined directly). (For the analysis of KOH, a suitable sample weight is 50 g. of 100% KOH.)

## DETERMINATION OF TOTAL ALKALINITY OF SODIUM HYDROXIDE

The total alkalinity of sodium hydroxide is best determined by addition of an excess of a strong acid, boiling to remove carbon dioxide, and back-titration with a strong base to a visual end point.

**Procedure.**—Transfer a 50-ml. aliquot of the NaOH sample solution to a 500-ml. conical flask; add a few drops of methyl red indicator solution and a slight excess (of about 2 ml.) of 1 N H<sub>2</sub>SO<sub>4</sub>. Place a powder funnel in the flask mouth and



boil the solution gently for 5 minutes. Cool, rinse down the flask walls with water, and titrate the excess of acid with 0.1 N NaOH, adding more methyl red if necessary. (In precision work, correct the titrant volumes for temperature and the buret calibration.) Compare the NaOH and  $\text{H}_2\text{SO}_4$  solutions in a separate titration, and let  $F$  = ml. of  $\text{H}_2\text{SO}_4$  equivalent to exactly one ml. of NaOH. The % Total Alkalinity as  $\text{Na}_2\text{O}$  = (ml. of  $\text{H}_2\text{SO}_4$  - ml. of NaOH  $\times F$ )  $\times$  (normality of  $\text{H}_2\text{SO}_4$ )  $\times 0.030990 \times 100 \div$  (weight of sample in g. represented by aliquot). Where of interest, the result may be expressed as NaOH or  $\text{Na}_2\text{CO}_3$ ; the respective factors being 0.039997 and 0.052994. (In the analysis of KOH, the respective factors for  $\text{K}_2\text{O}$ , KOH, and  $\text{K}_2\text{CO}_3$  are 0.047102, 0.056109, and 0.069107.)

### DETERMINATION OF CARBONATE CONTENT OF SODIUM HYDROXIDE

For the determination of carbonate in sodium hydroxide, the gas analysis method is to be preferred, especially when only a small amount of carbonate is present. For the occasional determination (and where a large amount of carbonate is present), a titrimetric approach is feasible. This is based on the titration of the sodium hydroxide content with standard acid with carbonate precipitated as barium carbonate. The difference in this titration result and that for the total alkalinity corresponds to carbonate.

**Gas Analysis Procedure for Carbonate.**—Transfer a 50-ml. aliquot of the NaOH sample solution (or a larger aliquot if the carbonate content is quite small) to the sample receptacle of the apparatus (Fig. 12-17, Vol. I, page 303), and proceed as given in Vol. I on pages 302-306. As indicated on page 306, express the result as %  $\text{Na}_2\text{CO}_3$  in the original NaOH sample. (In the analysis of KOH, express the result as %  $\text{K}_2\text{CO}_3$ .) The % Actual NaOH = % Total Alkalinity as  $\text{Na}_2\text{O}$   $\times 1.2907$  - %  $\text{Na}_2\text{CO}_3 \times 0.75474$ . (For the analysis of KOH, the factors in the corresponding equation have the values 1.1912 and 0.81192.)

**Titrimetric Procedure for Hydroxide in Sodium Hydroxide (Indirect Determination of Sodium Carbonate).**—In a white porcelain casserole, treat a 50 ml. aliquot of the NaOH sample solution with 50 ml. of a 10%  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  solution, which has been neutralized to the faint pink of added phenolphthalein. Stir gently and titrate with 1 N HCl to the disappearance of the pink color.

From the titration result, the % Actual NaOH = (ml. of HCl)  $\times$  (normality of HCl)  $\times 0.039997 \times 100 \div$  (weight of sample in g. represented by aliquot). (For KOH, the factor is 0.056109.) The %  $\text{Na}_2\text{CO}_3$  = % Total Alkalinity as  $\text{Na}_2\text{O}$   $\times 1.7101$  - % NaOH  $\times 1.3250$ . (For the analysis of KOH, the factors in the corresponding equation have the values 1.4672 and 1.2316.)

### DETERMINATION OF CHLORIDE IN SODIUM HYDROXIDE

Chloride may be determined in sodium hydroxide by a conventional Volhard titration (see Vol. I, page 329) employing a 100-ml. aliquot of the prepared Sodium Hydroxide Sample Solution (page 601). The result is often expressed as % NaCl (or in the analysis of potassium hydroxide as % KCl).

### DETERMINATION OF SULFATE IN SODIUM HYDROXIDE

Sulfate is usually determined in sodium hydroxide by the conventional gravimetric barium sulfate procedure (see Vol. I, pages 1007-1008) after initial solution and acidification of a suitable sample of the sodium hydroxide (25 g. of 100%

NaOH). The result is often expressed as  $\% \text{Na}_2\text{SO}_4 = (\text{g. of ignited BaSO}_4) \times 0.6086 \times 100 \div (\text{sample weight in g.})$ . (In the analysis of potassium hydroxide the result is expressed as  $\text{K}_2\text{SO}_4$  and the factor has the value 0.7466.) Where iron and aluminum are present in unusually large amounts, their prior precipitation from ammoniacal solution and separation may be desirable.

### DETERMINATION OF CHLORATE IN SODIUM HYDROXIDE

Chlorate may be present in sodium hydroxide produced electrolytically and in the cell liquors. Its determination is usually based on addition of an excess of a reducing agent and a redox titration of the excess. One suitable procedure involves reduction with arsenite and a cerate titration of the excess of arsenite, the reactions being catalyzed by the addition of osmium tetroxide.

**Procedure.**<sup>104</sup>—Transfer a 50-ml. aliquot of the NaOH sample solution to a 500-ml. conical flask and add from a buret an excess of 0.01 *N* (i.e., 0.005 *M*)  $\text{NaAsO}_2$  (neutralized and made about 2.5% in  $\text{NaHCO}_3$ ). Now add 5 drops of 0.01 *M*  $\text{OsO}_4$  in 0.1 *N*  $\text{H}_2\text{SO}_4$ . Dilute to a volume of 300 ml. with water. Warm to 60°C., add 2 drops of iron(II)-*o*-phenanthroline complex, and titrate with 0.01 *N* (i.e., 0.01 *M*) cerate solution in sulfuric acid, maintaining a temperature between 40 and 60°C., to a faint blue end point. Similarly titrate the same volume of  $\text{NaAsO}_2$  solution, omitting the sample.  $\% \text{ClO}_3 = (\text{ml. of cerate solution consumed by sample} - \text{ml. of cerate solution consumed without sample}) \times (\text{normality of cerate solution}) \times 0.01391 \times 100 \div (\text{sample weight in g. represented by aliquot taken})$ . Alternatively the result may be expressed as  $\% \text{NaClO}_3$  by use of the factor 0.01774. (For  $\% \text{KClO}_3$  the factor is 0.02043.)

**Remarks.**—The aliquot size and the amount of  $\text{NaAsO}_2$  solution added may be adjusted according to the chlorate content. By the addition of silver ion, as well as osmium tetroxide, it has been reported that the determination can be effected without heating.<sup>105</sup>

### DETERMINATION OF NICKEL IN SODIUM HYDROXIDE

The presence of appreciable amounts of nickel, copper, manganese (and to some extent iron) in sodium hydroxide may render it unsuited to the production of viscose rayon or of a stable sodium hypochlorite solution. Nickel may be encountered in various grades of sodium hydroxide from about 0.01% to below 1 part per million. The method of analysis selected will therefore depend on the expected level. For the upper region, a photometric method is satisfactory including a diethyldithiocarbamate procedure employing a preliminary dimethylglyoxime extraction. At the parts per million range a spectrographic method may be preferred for routine control (see page 607).

**Photometric Diethyldithiocarbamate Procedure for Nickel.**<sup>106</sup>—Place a 100-ml. aliquot of the NaOH Sample Solution for Trace Metal Analysis (page 601) in a separatory funnel, add 20 ml. of citrate buffer *A* (for preparation, see below). Now add concentrated aqua ammonia until the solution is neutral to litmus and then 1 ml. in excess. Add 10 ml. of a 0.1% ethanolic dimethylglyoxime solution and 20 ml. of (metal-free) chloroform. Shake 1 minute, allow phase separation, and

<sup>104</sup> Based on a procedure recommended by Solvay Process Div., Allied Chem. Corp.

<sup>105</sup> Csányi, L. J., and Szabó, M., *Talanta*, **1**, 359, 1958.

<sup>106</sup> Based in part on a procedure recommended by Solvay Process Div., Allied Chem. Corp.

drain as much of the chloroform layer as possible into a second separatory funnel containing 20 ml. of 2.5% aqua ammonia and 30 ml. of water. Repeat the extraction with 10 ml. of chloroform. Shake the combined extracts in the second funnel for 1 minute, allow phase separation, and suck off the aqueous layer and discard it. Wash the chloroform phase twice with water. Now add 25 ml. of 1 *N* HCl, shake, allow phase separation, and separate and discard the organic layer. Add a few ml. of carbon tetrachloride to the funnel, shake for 15 seconds (to separate chloroform), and draw off the solvent as completely as possible. Add 10 ml. of citrate buffer *B* (see below for preparation) and concentrated aqua ammonia until the solution is neutral to litmus and then 1 ml. in excess. Add exactly 20 ml. of isoamyl alcohol and 10 ml. of a 0.2% sodium diethyldithiocarbamate solution in water (store in a refrigerator; prepare fresh every 3 weeks). Shake for 2 minutes, allow to stand for 5 minutes, and slowly draw off the lower, aqueous phase. (The organic phase should be clear.)

Similarly carry a 100-ml. aliquot of the Acid Reagent Blank for Trace Metal Analysis (page 601) through the above extraction scheme and retain the final diethyldithiocarbamate-isoamyl alcohol phase.

Measure the absorbance of the final extract from both the sample and the blank against water at 390 millimicrons (or employ a filter transmitting in this region). Subtract the absorbance of the blank from that of the sample, and read the result from a calibration curve prepared by carrying known amounts of an acidic  $\text{NiSO}_4$  solution through the procedure.

**Preparation of Citrate Buffers.**—To prepare citrate buffer *A*, dissolve 200 g. of diammonium citrate in 600 ml. of water and adjust to pH 9–9.5 with aqua ammonia (pH-meter). Add 10 ml. of 0.1% ethanolic dimethylglyoxime solution and extract 3 times with 10 ml. portions of chloroform. Filter the aqueous layer and dilute to exactly 1000 ml. with water.

To prepare citrate buffer *B*, proceed similarly but substitute 10 ml. of a 0.2% sodium diethyldithiocarbamate solution in water for the dimethylglyoxime solution and perform the extraction with 20-ml. portions of carbon tetrachloride until the organic phase is no longer colored.

**Remarks.**—The above procedure is somewhat tedious as a two-step extraction is involved. An  $\alpha$ -furildioxime procedure employing a single extraction with chloroform and with iron(III) masked by citrate may offer superior sensitivity and excellent selectivity.<sup>107</sup>

## DETERMINATION OF COPPER IN SODIUM HYDROXIDE

Copper in trace amounts in sodium hydroxide may be determined spectrophotometrically. Some workers prefer a diethyldithiocarbamate procedure (essentially that given in Vol. 1, page 407); however, a Neocuproin (i.e., 2,9-dimethyl-1,10-phenanthroline) procedure offers greater sensitivity and less interference from nickel and iron.<sup>108</sup> Alternatively copper may be determined spectrographically (see page 607).

**Neocuproin Procedure for Copper.**—Evaporate a 100-ml. aliquot of the NaOH Sample Solution for Trace Metal Analysis (page 601), or a larger aliquot if necessary, to dryness with a few drops of  $\text{HNO}_3$  added. Dissolve the residue in water, dilute to a volume of about 150 ml. with water and transfer with water rinses to

<sup>107</sup> Mains, F., and Raggett, R. E., *Chemist-Analyst*, 50, 4, 1961.

<sup>108</sup> Mains, F., and Raggett, R. E., *Chemist-Analyst*, 50, 4, 1961.

a 300-ml. separatory funnel. Add 10 ml. of a 10% potassium sodium tartrate solution and 1 ml. of a 10% hydroxylammonium chloride solution, and shake well. Add concentrated aqua ammonia dropwise until the solution is neutral to litmus. Add 40 ml. of 0.025% Neocuproin solution in 1-butanol. Shake, allow the phases to separate, drain the aqueous layer, and transfer a portion of the organic phase to a tube cuvet and centrifuge for 5 minutes to separate any suspended water. Measure the absorbance at 450 millimicrons versus water. Carry 100 ml. of the Acid Reagent Blank for Trace Metal Analysis (page 601) through the full procedure and subtract its absorbance from that of the sample preparation. Calculate the results from a calibration curve obtained by carrying a sodium hydroxide solution with known amounts of copper through both the sample preparation step and the above procedure.

### DETERMINATION OF MANGANESE IN SODIUM HYDROXIDE

Manganese in trace amounts in sodium hydroxide may be determined spectrophotometrically after the periodate oxidation method of Williard and Greathouse (see also Vol. I, page 653). Alternatively, a spectrographic procedure is feasible (see page 607).

*Photometric Permanganate Procedure.*—Place a suitable sample (10 g. of 100% NaOH) in a conical flask and dissolve and dilute in water to a volume of about 50 ml. Cautiously add 30 ml. of 50%  $\text{H}_2\text{SO}_4$ , heat over a flame or hot plate with swirling until  $\text{SO}_3$  fumes appear. Allow the residue to cool, add cautiously 30 ml. of water, and warm to effect solution. Filter through paper, thus removing silica, and collect the filtrate in a conical flask. Rinse the filter with hot water until the combined filtrate has a volume of about 100 ml. Add 0.4 g. of potassium metaperiodate or sodium paraperiodate. Digest near the boiling point for about 30 minutes. Cool, dilute exactly to 100 ml., transfer a portion to a cuvet, and measure the absorbance versus water at 522 millimicrons or employing a suitable filter. Read the result from a standard curve prepared by carrying known amounts of manganese through the procedure.

*Remarks.*—For visual comparison procedure, the total solution after cooling is transferred to a 100-ml. Nessler tube and compared with standards (which are stable for weeks or even months if prepared after the procedure). If large amounts of iron are present, phosphoric acid may be added with the sulfuric acid.<sup>109</sup>

### DETERMINATION OF IRON IN SODIUM HYDROXIDE

Where iron is encountered in large amounts with silica, aluminum, etc., in extremely crude sodium hydroxide, it may be determined within the framework of a scheme for the separation and determination of these various impurities (see page 606). In less crude products, iron may be determined directly by an *o*-phenanthroline procedure, employing hydroxylamine as the reductant (preferably with heating to speed the reduction) and in the presence of citrate (see vol. I, page 553). For this determination a suitable aliquot (50 ml.) of the Sodium Hydroxide Solution for Trace Metal Analysis (page 601) may be employed.

### DETERMINATION OF CALCIUM IN SODIUM HYDROXIDE

Where large amounts of calcium are encountered in crude sodium hydroxide the determination may be part of the integrated scheme for the separation and de-

<sup>109</sup> Mehlig, J. P., Ind. Eng. Chem., Anal. Ed., 11, 274, 1939; Williams, D., and Andes, R. G., *ibid.*, 17, 28, 1945.

termination of various impurities (see below) or may be determined directly by an ethylenediaminetetraacetate titration at pH 12–12.5 employing a suitable metal indicator (e.g., murexide, Calcon, calcein) essentially after the procedure in Vol. I, page 265, omitting a tungstate separation, with iron and aluminum masked by the addition of adequate amounts of cyanide and triethanolamine. Where only small amounts of calcium are encountered (2–15 parts per million), a prior concentration of calcium is required. The use of the Dowex chelating resin A-1 for this purpose is elegant, since any heavy metals also concentrated can be masked in the subsequent ethylenediaminetetraacetate titration of calcium in the eluate.<sup>110</sup>

**Procedure for Separation and Determination of Trace Calcium.**—Stir about 50 g. of Dowex chelating resin A-1 (as received in the Na form) with 50 ml. of 2 N HCl, allow to settle, decant the acid, and wash the resin with water. Now stir with 50 ml. of 2 N NaOH and allow to stand for 15 minutes (the resin volume almost doubles). Place the resin, now in the Na form, in a 15-cm. column on top of a borosilicate wool plug to a height of 10 cm. Wash the column with water until the effluent is free of alkali. After use, the resin may be regenerated *in situ* to the Na form by the slow passage of 2 N NaOH followed by rinsing of the column with water. The resin column must be covered with liquid at all times.

Dilute or dissolve a suitable sample of the NaOH (25 g. of 100% NaOH) with about 100 ml. of water, and just neutralize with 12 N HCl to litmus. Dilute to a volume of about 250 ml. and pass the solution through the chelating resin column (Na form) at a rate of 2 ml. per minute. Now pass 100 ml. of water. Discard these effluents. Elute the calcium with 25 ml. of 2 N HCl and wash with 50 ml. of water, collecting the eluate and washings in a single beaker. Add 10 ml. of reagent grade triethanolamine and 30 ml. of 2 N NaOH solution, and dilute to a volume of about 200 ml. with water. Add a suitable metal (calcium) indicator (e.g., 50 mg. of a 5:3:500 ground mixture of calcein, thymolphthalein, and sodium chloride) and titrate with a 0.02 M solution of disodium ethylenediaminetetraacetate (EDTA) from a microburet to the end point. In the same manner, titrate 30 ml. of the 2 N NaOH solution as a blank. The % Ca = (ml. of EDTA required for sample – ml. of EDTA for blank)  $\times$  (molarity of EDTA)  $\times$  0.04008  $\times$  100  $\div$  (sample weight in g.).

**Remarks.**—The Dowex chelating resin A-1 offers salient possibilities for the concentration of other trace elements from salt solutions, such as are obtained by the simple neutralization of common acids and bases.<sup>111</sup>

## DETERMINATION OF VARIOUS IMPURITIES IN SODIUM HYDROXIDE

In the analysis of extremely crude sodium hydroxide, the determination of silica, aluminum, iron, calcium, and magnesium, may be integrated into a separation scheme,<sup>112</sup> which in essence parallels the classic approach to the analysis of these substances in gypsum (see Vol. I, page 273). A suitable sample of the alkali (50 g. of 100% NaOH or KOH) is dehydrated by hydrochloric acid evaporations, silica is separated, and ignited and weighed in the usual manner. (If an appreciable residue remains after a hydrofluoric acid volatilization, it is fused with potassium bisulfate, dissolved in acidified water, and combined with the filtrate from the

<sup>110</sup> Van der Reyden, A. J., and van Lingen, R. L. M., *Z. anal. Chem.*, **187**, 241, 1962.

<sup>111</sup> For literature, see data sheet on product, J. T. Baker Chem. Co.

<sup>112</sup> For full procedural details, see Solvay Process Division, Allied Chem. Corp., Bull. No. 9, *The Analysis of Alkalies*, 1961, 80 pp.

silica separation.) Aluminum and iron are separated by an ammoniacal precipitation, ignited to oxides, and weighed. Iron is subsequently determined and aluminum is found by difference. Calcium and magnesium in the filtrate from the ammoniacal separation are determined by gravimetric oxalate and pyrophosphate methods. Of course, ethylenediaminetetraacetate titrations may be substituted for the determination of calcium and magnesium and possibly of iron and aluminum as well. Where iron and calcium are present in only small amounts, they may be determined directly (see above). Where silica is present in only small amounts, a molybdenum blue photometric procedure is suitable (see Vol. I, page 962).<sup>113</sup>

For the application of sodium hydroxide in the nuclear industry, the trace boron content may be of interest and determined, after acidification, by a methyl borate distillation procedure followed by the photometric determination of borate (see Vol. I, pages 233–235). In one study special distillation conditions have been recommended and the use of curcumin as the chromogenic agent.<sup>114</sup>

For the analysis of pharmaceutical grade and reagent grade sodium hydroxide, relevant monographs should be consulted (*U. S. Pharmacopeia* and works cited in the footnote on page 552).

### SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN SODIUM HYDROXIDE

Direct spectrographic methods using an internal standard, often molybdenum, are frequently employed in the control of the production of alkali metal hydroxides and carbonates. The procedures published by the American Society for Testing Materials are applicable.<sup>115</sup>

### POTASSIUM HYDROXIDE

Potassium hydroxide (caustic potash), KOH, is offered in the technical and commercial grades in various physical forms ranging in composition from 73 to 96% KOH, of which the product 92% KOH nominal is the most common. The *U. S. Pharmacopeia* recognizes a product containing not less than 85% total alkali as KOH and including not more than 3.5%  $K_2CO_3$ . Reagent grade potassium hydroxide, meeting American Chemical Society specifications, contains not less than 85% KOH, and is also available in a low-chloride form ( $<0.005\%$  Cl). It should be recognized that in all grades, water is present and accounts principally for the low potassium hydroxide content. A 45% aqueous solution of potassium hydroxide is available in both the technical and reagent grades.

The analysis of potassium hydroxide, other than for sodium content, is identical to that of sodium hydroxide; hence, the appropriate factors for potassium hydroxide have been included parenthetically in the procedures for sodium hydroxide (see above). Since commercial potassium compounds contain appreciable amounts of sodium, the determination of sodium in potassium hydroxide is of interest; the usual procedure, involving removal of the bulk of potassium as the perchlorate and the gravimetric determination of sodium as the magnesium uranyl acetate, is given in Vol. I, page 16.

<sup>113</sup> See also Kenyon, O. A., and Bewick, H. A., *Anal. Chem.*, 25, 145, 1953.

<sup>114</sup> United Kingdom Atomic Energy Authority, PG Rept. 85(W), *Analytical Methods for the Inspection of Solid Sodium Hydroxide and Caustic Liquor*, H. M. Stationery Office, London, 1960.

<sup>115</sup> Am. Soc. for Testing and Materials, *Methods for Emission Spectrochemical Analysis*, 3rd Ed., Philadelphia, 1960, 476–8; 502–7.

## SODIUM CARBONATE

Sodium carbonate (soda ash, calcined soda, "ash," "soda"),  $\text{Na}_2\text{CO}_3$ , is offered principally in the anhydrous form containing nominally 58%  $\text{Na}_2\text{O}$  (99%  $\text{Na}_2\text{CO}_3$ ), and as the monohydrate (crystal carbonate) containing nominally 48%  $\text{Na}_2\text{O}$  (82%  $\text{Na}_2\text{CO}_3$ ). The anhydrous product is offered in both a light and dense form ("light ash" and "dense ash"); the latter is sometimes produced with a higher calcium content. (For consideration of sodium sesquicarbonate and modified sodas, see below.) Sodium carbonate decahydrate (sal soda, washing soda, soda crystals, natron),  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , is also offered commercially. The *U. S. Pharmacopoeia* recognizes a monohydrate form containing 99.5% minimum  $\text{Na}_2\text{CO}_3$  on a dried basis. Reagent grade sodium carbonate, meeting American Chemical Society specifications, is available in the anhydrous and monohydrate forms. For the analysis of the pharmaceutical and reagent products, relevant monographs should be consulted (*U. S. Pharmacopoeia* and works cited in the footnote on page 552). Since the analysis of potassium carbonate parallels that of sodium carbonate, factors for the former are given parenthetically in the following procedures.

## SAMPLING OF SODIUM CARBONATE

For the analysis of sodium carbonate, a Sodium Carbonate Sample Solution and a Sodium Carbonate Sample Solution for Trace Metal Analysis are prepared in the same manner as the corresponding sodium hydroxide solutions (page 601), but employing sample weights of 45 g. and 50 g. of 100%  $\text{Na}_2\text{CO}_3$ , respectively. (Similar sample weights are employed in the analysis of potassium carbonate.)

## DETERMINATION OF TOTAL ALKALINITY OF SODIUM CARBONATE

For the determination of the total alkalinity of sodium carbonate, the procedure is identical to that for sodium hydroxide. The result may be expressed as %  $\text{Na}_2\text{CO}_3$  or as %  $\text{Na}_2\text{O}$ . Where the bicarbonate content has been determined (see below), the % Actual  $\text{Na}_2\text{CO}_3$  = % Total Alkalinity as  $\text{Na}_2\text{CO}_3$  - %  $\text{NaHCO}_3 \times 0.63083$  or % Actual  $\text{Na}_2\text{O}$  = % Total Alkalinity as  $\text{Na}_2\text{O}$  - %  $\text{NaHCO}_3 \times 0.36889$ . (For the analysis of potassium carbonate, % Actual  $\text{K}_2\text{CO}_3$  = % Total Alkalinity as  $\text{K}_2\text{CO}_3$  - %  $\text{KHCO}_3 \times 0.69025$ .)

## DETERMINATION OF SODIUM BICARBONATE IN SODIUM CARBONATE

The determination of bicarbonate in sodium carbonate is usually based on the addition of a sufficient amount of sodium hydroxide to convert bicarbonate to carbonate, precipitation of barium carbonate by the addition of barium chloride, and back-titration of the excess of sodium hydroxide to the disappearance of the pink color of phenolphthalein. The classical procedure (Winkler's method) can be modified to give more satisfactory precision, especially where only a small amount of bicarbonate is present, by substitution of a potentiometric end point.<sup>116</sup> For routine process control, bicarbonate may be estimated, especially where a large amount is present, by a direct titration with sodium hydroxide using silver nitrate as an external indicator.

<sup>116</sup> Regier, R. B., *Anal. Chem.*, 19, 1039, 1947; see also ASTM std. D501.

**Visual Titration Procedure.**—Transfer a 50-ml. aliquot of the  $\text{Na}_2\text{CO}_3$  Sample Solution to a conical flask. Add 0.1 *N* ( $\text{CO}_2$ -free)  $\text{NaOH}$  in slight excess ( $>1$  ml.) of that required by the  $\text{NaHCO}_3$  present and 300 ml. of 10%  $\text{BaCl}_2$  solution (neutralized to a faint pink color after addition of some phenolphthalein). Without separation of the precipitate and with continuous stirring, titrate the excess of  $\text{NaOH}$  with 0.1 *N*  $\text{HCl}$  to the decolorization of the phenolphthalein. Then titrate the same amount of  $\text{NaOH}$  solution with the  $\text{HCl}$  solution in the presence of the same amount of  $\text{BaCl}_2$  solution (or rely on the established normalities); let  $F$  = ml. of  $\text{NaOH}$  equivalent to exactly 1 ml. of  $\text{HCl}$ . Then  $\% \text{NaHCO}_3 = (\text{ml. of NaOH added} - \text{ml. of HCl consumed by sample} \times F) \times (\text{normality of NaOH}) \times 0.084007 \times 100 \div (\text{sample weight in g. represented by the aliquot taken})$ . (For  $\% \text{KHCO}_3$  the factor is 0.10012.)

**Remarks.**—Some workers prefer, after the volume of  $\text{NaOH}$  required to convert all  $\text{NaHCO}_3$  in the sample to  $\text{Na}_2\text{CO}_3$  has been calculated from the experimental result, actually to add this amount to a further aliquot of the Sample Solution under the titration conditions, and, if necessary, conduct a further titration with  $\text{HCl}$ . As in the potentiometric titration procedure, given below, it is also possible to employ a known weight of bicarbonate-free  $\text{Na}_2\text{CO}_3$  in the second titration, thus more closely duplicating the conditions in the titration of the sample.

**Potentiometric Titration Procedure.**—Place a 50-ml. aliquot of the  $\text{Na}_2\text{CO}_3$  Sample Solution in a 250-ml. beaker. Add exactly 5 ml. of 0.1 *N*  $\text{NaOH}$  from a pipet and 100 ml. of a 10%  $\text{BaCl}_2$  solution (122 g. of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  dissolved and diluted with water to 1000 ml. and neutralized to added phenolphthalein). Insert the calomel-glass electrode pair of a pH-meter in the solution and titrate promptly with 0.1 *N*  $\text{HCl}$  while stirring continuously. When the pH changes, record the readings after each addition of a 0.1-ml. increment of  $\text{HCl}$ . Now in the same manner titrate a weight *equal* to that of the sample (represented by the aliquot of the sample solution taken) of bicarbonate-free  $\text{Na}_2\text{CO}_3$  (prepared by ignition of  $\text{Na}_2\text{CO}_3$  of reagent grade or preferably of a portion of the sample itself at  $200^\circ\text{C}$ . overnight or at  $250^\circ\text{C}$ . for a shorter time). Plot pH *versus* ml. of  $\text{HCl}$  for the titration of the sample and the bicarbonate-free  $\text{Na}_2\text{CO}_3$  on the same coordinates. The difference between the inflection points of the two curves corresponds to the bicarbonate content of the sample. The  $\% \text{NaHCO}_3 = (\text{ml. of HCl required by sample} - \text{ml. of HCl required by the bicarbonate-free Na}_2\text{CO}_3) \times (\text{normality of HCl}) \times 0.084007 \times 100 \div (\text{sample weight in g. represented by the aliquot taken})$ . (The factor for  $\% \text{KHCO}_3$  is 0.10012.)

**External Indication Procedure.**—Transfer a 50-ml. aliquot of the  $\text{Na}_2\text{CO}_3$  Sample Solution to a 250-ml. beaker. Titrate with 1.0 *N*  $\text{NaOH}$  until 1 drop of the solution added to a drop of a freshly prepared 10%  $\text{AgNO}_3$  solution in water on a white spot plate gives a dark color instantly (due to the formation of hydrous  $\text{Ag}_2\text{O}$ ). The  $\% \text{NaHCO}_3 = (\text{ml. of NaOH}) \times (\text{normality of NaOH}) \times 0.0840 \times 100 \div (\text{weight of sample in g. represented by the aliquot taken})$ .

**Remark.**—Some degree of experience is required in the recognition of the end point before satisfactory results can be secured. This procedure is unsuitable for referee analysis or where only a small amount of bicarbonate is present.

## DETERMINATION OF IMPURITIES IN SODIUM CARBONATE

All procedures for the determination of impurities in sodium hydroxide are applicable to sodium carbonate without serious modification (chlorate and manganese



are seldom required). For the determination of chloride, the aliquot of the sample solution taken will depend on the purity and source of the sodium carbonate sample, that is, on its chloride content. Where of interest, the loss of weight on drying at 250°C. for 2 hr. (or better at 285°C.) is determined and, based on the content of sodium bicarbonate (which is converted on heating to  $\text{Na}_2\text{CO}_3$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ ), the free water present is calculated: The % Free  $\text{H}_2\text{O}$  = % Loss in Weight on Heating - %  $\text{NaHCO}_3 \times 0.3692$ . Further, the volatile matter at 150–155°C. (1 hr.) may be determined.

The determination of "matter insoluble in water" for sodium carbonate (and, where of interest, generally for alkali hydroxides, carbonates, modified sodas, etc.) is effected by dissolving a suitable sample (20–50 g.) in 300 ml. of water, filtering through a dry, tared Gooch or sintered glass funnel, washing the filter with water until free of alkali, drying at 110°C., and weighing. (Some organizations prefer to bring the solution to boiling before the filtration; however, the possibility of weight loss by the crucible on the passage of the hot alkaline solution should be recognized.)

Trace sulfate in sodium carbonate may be determined by a sulfide evolution method (see page 567).

A special extraction procedure has been devised for the determination of trace oil in sodium carbonate.<sup>117</sup>

### SODIUM BICARBONATE

Sodium bicarbonate (sodium acid carbonate, baking soda),  $\text{NaHCO}_3$ , is offered principally in the pharmaceutical grade, meeting the requirements of the *U. S. Pharmacopeia* (95–105%  $\text{NaHCO}_3$ , but typically 99.8–99.9%). High assay material is also available in the technical grade. The reagent grade product, meeting the specifications of the American Chemical Society, contains 99.7–100.3%  $\text{NaHCO}_3$ . For the analysis of the pharmaceutical grade and reagent grade products, relevant monographs should be consulted (*U. S. Pharmacopeia* and the works cited in the footnote on page 552). For these grades, the assay is based on the direct titration of the dried sample with either sulfuric or hydrochloric acid to the methyl orange end point. A further approach based on the thermal decomposition of the sample finds use. Employing a train, the loss in weight on heating at 250°C. and the weight of the evolved carbon dioxide (absorbed in soda-asbestos) are determined. From the results, the %  $\text{NaHCO}_3$ , %  $\text{Na}_2\text{CO}_3$ , and % Free  $\text{H}_2\text{O}$  are calculated.<sup>118</sup> The determination of "matter insoluble in water" is accomplished as described for sodium carbonate.

### POTASSIUM CARBONATE

Potassium carbonate (potash),  $\text{K}_2\text{CO}_3$ , is available in the technical grade in the nominal compositions 80–85, 85–95, 90–95, and 96–99%  $\text{K}_2\text{CO}_3$  (the remainder being largely water). The sesquihydrate,  $\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$  (85.3%  $\text{K}_2\text{CO}_3$ ) is encompassed by the 80–85% material. In the technical grade, an aqueous solution containing 47%  $\text{K}_2\text{CO}_3$  minimum is also offered. The *National Formulary* recognizes a product containing 99%  $\text{K}_2\text{CO}_3$  minimum after drying for 4 hours at 180°C. Reagent grade potassium carbonate, meeting American Chemical Society

<sup>117</sup> For procedure, see Solvay Process Div., Allied Chem. Corp. Bull., No. 9, The Analysis of Alkalies, 1961, 80 pp.

<sup>118</sup> For a suitable apparatus assembly and for procedural details see ASTM std. D501.

specifications, is available in an anhydrous form and as the sesquihydrate. For the analysis of pharmaceutical grade and reagent grade potassium carbonate relevant monographs should be consulted (*U. S. Pharmacopeia* and works cited in footnote 27 on page 552).

The analysis of technical grade potassium carbonate is essentially identical to that of sodium carbonate (and the relevant factors are included in the sodium carbonate procedures given above). Total alkalinity is determined and, if the product contains potassium bicarbonate, this is determined by one of the procedures given for titrimetric determination of sodium bicarbonate in sodium carbonate. Alternatively, if the product contains potassium hydroxide, this is determined essentially by the procedure for the determination of sodium hydroxide in sodium hydroxide (that is, with carbonate precipitated as barium carbonate, page 602), but employing 300 ml. of the barium chloride solution and performing the titration with 0.1 *N* hydrochloric acid.

In the preparation of the Potassium Carbonate Sample Solution for Trace Metal Analysis, analogous to the similar solution for sodium hydroxide, a sample weight of 65 g. of 100%  $K_2CO_3$  is usually suitable. Impurities commonly determined in potassium carbonate include chloride, iron, copper, nickel, and chlorate. The loss in weight on drying at 250°C. (or better at 285°C.) is also frequently determined.

Where the sodium content is of interest, it may be determined by the removal of the bulk of potassium as the perchlorate and the gravimetric determination of sodium as the magnesium uranyl acetate as given in Vol I, page 16.

### MODIFIED SODAS

Sodium sesquicarbonate (trona, natrona, "modified soda," laundry soda),  $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ , is offered in a commercial grade as are other mixtures of sodium bicarbonate and sodium carbonate which are all termed sesquicarbonate-type modified sodas. The analysis of these products parallels that of sodium carbonate. Common determinations include total alkalinity expressed as  $Na_2O$ , sodium bicarbonate, sodium carbonate (by difference), and sodium chloride; matter insoluble in water is determined sometimes as well. Because of the large bicarbonate content, its direct titration with sodium hydroxide using silver nitrate as an external indicator often affords sufficient accuracy for routine control purposes. Where sufficient ammonium salts are present in the product to warrant their determination, digestion with sulfuric acid after Kjeldahl, distillation, and titration of collected ammonia is usually employed (Vol. I, page 740). In order to report the results on a one hundred per cent basis, water is often calculated by subtracting the sum of the percentages of the major constituents from 100%.

### MIXTURES OF SODIUM HYDROXIDE AND CARBONATE (SUPER ALKALIES)

Mixtures containing sodium hydroxide and sodium carbonate are often termed super alkalies and are offered in various commercial formulations. For these products, often only the major constituents are determined. Where of interest, impurities may be determined by the procedures given for sodium hydroxide. The preparation of the Sample Solution and the determination of the total alkalinity (expressed as %  $Na_2O$ ) follow the procedures given for sodium hydroxide. The procedure for the determination of sodium hydroxide in sodium hydroxide (with

carbonate precipitated as barium carbonate, page 602) is applicable, but a 25-ml. aliquot of the Super Alkali Sample Solution and 100 ml. of the barium chloride solution are employed. The results are usually expressed as %  $\text{Na}_2\text{CO}_3$  and %  $\text{NaOH}$ . The %  $\text{Na}_2\text{CO}_3 = (\% \text{ Total Alkalinity Expressed as } \text{Na}_2\text{O} - \% \text{ NaOH} \times 0.7748) \times 1.7101$ .

## ALKALINE DETERGENTS AND OTHER BASES

The analysis of mixed bases, including alkali metal hydroxides, carbonates, silicates, phosphates and borates is beyond the scope of this chapter. For the analysis of alkali metal phosphates, consult Vol. I, Chapter 35, and also ASTM standards D501, D538, and D595. For the analysis of alkali metal hydroxides, carbonates, and their mixtures, see the relevant Solvay bulletin<sup>119</sup> and ASTM standards D501, D456, D457, D458, and D928. For the analysis of detergents containing alkali metal borates and silicates, see ASTM standards D501, D537, D594, and D929.

## SPECIFIC GRAVITY-COMPOSITION TABLES

### INTRODUCTION

In the following tables the Degrees Baumé (Heavy) and Degrees Twaddell are given for 60°F. and are related to the specific gravity at exactly 60°F. compared to water at the same temperature as follows:

$$\text{Degrees Baumé, Heavy} = 145 - (145/\text{Specific Gravity})$$

$$\text{Degrees Twaddell} = (\text{Specific Gravity} - 1) \times 200$$

With some tables, allowances are given for correcting the °Bé. to other temperatures (the correction being added to the observed value on the hydrometer for a temperature above 60°F., and subtracted for below 60°F.)

Aqua ammonia, since it has values for the specific gravity below 1.0 is expressed in Degrees Baumé, Light, which is related at 60°F. to the specific gravity at exactly 60°F. compared to water at the same temperature as follows:

$$\text{Degrees Baumé, Light} = (140/\text{Specific Gravity}) - 130$$

For the use of hydrometers in the estimation of specific gravity, see page 534. The Baumé hydrometers used should be graduated by the formulae given above.

For the plant use of these tables, the following conversion factors, which neglect the change in the density of water with temperature, are useful:

$$\text{Specific gravity} \times 62.43 = \text{approx. lbs. of soln. per cu. ft.}$$

$$\text{Specific gravity} \times 8.345 = \text{approx. lbs. of soln. per U. S. gallon}$$

$$\text{Approx. lbs. of soln. per cu. ft.} \times \% (w/w) \times 0.01 = \text{approx. lbs. of solute per cu. ft.}$$

$$\text{Approx. lbs. of soln. per U. S. gallon} \times \% (w/w) \times 0.01$$

$$= \text{approx. lbs. of solute per U. S. gallon}$$

For further density data on common solutions, consult *International Critical Tables* or various handbooks.

<sup>119</sup> Solvay Process Div., Allied Chem. Corp. Bull., No. 9, The Analysis of Alkalies, 1961, 80 pp.

## SULFURIC ACID, 0-66°Bé.

degrees Baumé	sp. gr. 60/60°F.	degrees Twaddell	% w/w H <sub>2</sub> SO <sub>4</sub>	lbs. per cu. ft.	% w/w O.V.	lbs. O.V. per cu. ft.	Freezing pt., °F.
0	1.0000	0.0	0.00	62.37	0.00	0.00	32.0
1	1.0069	1.4	1.02	62.80	1.09	0.68	31.3
2	1.0140	2.8	2.08	63.24	2.23	1.41	30.5
3	1.0211	4.2	3.13	63.69	3.36	2.14	29.7
4	1.0284	5.7	4.21	64.14	4.52	2.90	28.9
5	1.0357	7.1	5.28	64.60	5.67	3.66	28.0
6	1.0432	8.6	6.37	65.06	6.84	4.45	27.0
7	1.0507	10.1	7.45	65.53	7.99	5.24	25.8
8	1.0584	11.7	8.55	66.01	9.17	6.06	24.6
9	1.0662	13.2	9.66	66.50	10.37	6.89	23.5
10	1.0741	14.8	10.77	66.99	11.56	7.74	22.3
11	1.0821	16.4	11.89	67.49	12.76	8.61	21.0
12	1.0902	18.0	13.01	68.00	13.96	9.49	19.4
13	1.0985	19.7	14.13	68.51	15.16	10.39	17.7
14	1.1069	21.4	15.25	69.04	16.36	11.30	16.3
15	1.1154	23.1	16.38	69.57	17.58	12.23	14.0
16	1.1240	24.8	17.53	70.10	18.81	13.19	12.0
17	1.1328	26.6	18.71	70.65	20.08	14.18	9.9
18	1.1417	28.3	19.89	71.21	21.34	15.20	7.7
19	1.1508	30.2	21.07	71.78	22.61	16.23	4.4
20	1.1600	32.0	22.25	72.35	23.87	17.27	+1.0
21	1.1694	33.9	23.43	72.94	25.14	18.34	-2.5
22	1.1789	35.8	24.61	73.53	26.41	19.42	-6.5
23	1.1885	37.7	25.81	74.13	27.69	20.53	-11.1
24	1.1983	39.7	27.03	74.74	29.00	21.68	-16.0
25	1.2083	41.7	28.28	75.36	30.34	22.87	-21.9
26	1.2185	43.7	29.53	76.00	31.69	24.08	-28.0
27	1.2288	45.8	30.79	76.64	33.04	25.32	-35.6
28	1.2393	47.9	32.05	77.30	34.39	26.58	-44.3
29	1.2500	50.0	33.33	77.96	35.76	27.88	-55.3
30	1.2609	52.2	34.63	78.64	37.16	29.22	-69.5
31	1.2719	54.4	35.93	79.33	38.55	30.58	-78.7
32	1.2832	56.6	37.26	80.03	39.98	32.00	-75.2
33	1.2946	58.9	38.58	80.74	41.40	33.42	-72.0
34	1.3063	61.3	39.92	81.47	42.83	34.90	-69.3
35	1.3182	63.6	41.27	82.22	44.28	36.41	-66.5
36	1.3303	66.1	42.63	82.97	45.74	37.95	-44.5
37	1.3426	68.5	43.99	83.74	47.20	39.53	-57.0
38	1.3551	71.0	45.35	84.52	48.66	41.13	-50.6
39	1.3679	73.6	46.72	85.32	50.13	42.77	-44.0

## SULFURIC ACID, 0-66°Bé. (Continued)

degrees Baumé	sp. gr. 60/60°F.	degrees Twaddell	% w/w H <sub>2</sub> SO <sub>4</sub>	lbs. per cu. ft.	% w/w O.V.	lbs. O.V. per cu. ft.	Freezing pt., °F.
40	1.3810	76.2	48.10	86.13	51.61	44.45	-38.2
41	1.3942	78.8	49.47	86.96	53.08	43.16	-33.0
42	1.4078	81.6	50.87	87.80	54.58	47.92	-28.6
43	1.4216	84.3	52.26	88.67	56.07	49.72	-25.5
44	1.4356	87.1	53.66	89.54	57.58	51.56	-22.8
45	1.4500	90.0	55.07	90.44	59.09	53.44	-20.9
46	1.4646	92.9	56.48	91.35	60.60	55.36	-19.3
47	1.4796	95.9	57.90	92.28	62.13	57.33	-19.1
48	1.4948	99.0	59.32	93.23	63.65	59.34	-19.8
49	1.5104	102.1	60.75	94.20	65.18	61.40	-22.0
50	1.5263	105.3	62.18	95.20	66.72	63.52	-25.4
51	1.5426	108.5	63.66	96.21	68.31	65.72	-29.6
52	1.5591	111.8	65.13	97.24	69.89	67.96	-34.2
53	1.5761	115.2	66.63	98.30	71.50	70.28	-36.0
54	1.5934	118.7	68.13	99.38	73.11	72.66	-39.5
55	1.6111	122.2	69.65	100.48	74.74	75.10	-45.0
56	1.6292	125.8	71.17	101.61	76.37	77.60	-40.8
57	1.6477	129.5	72.75	102.77	78.07	80.23	-39.4
58	1.6667	133.3	74.36	103.95	79.79	82.95	-28.4
59	1.6860	137.2	75.99	105.16	81.54	85.75	-9.0
60	1.7059	141.2	77.67	106.40	83.35	88.68	+11.5
61	1.7262	145.2	79.43	107.66	85.23	91.76	29.3
62	1.7470	149.4	81.30	108.96	87.24	95.06	39.5
63	1.7683	153.7	83.34	110.29	89.43	98.63	45.6
64	1.7901	158.0	85.66	111.65	91.92	102.63	44.8
64½	1.7957	159.1	86.33	112.00	92.64	103.75	42.9
64¾	1.8012	160.2	87.04	112.34	93.40	104.93	40.0
65	1.8068	161.4	87.81	112.69	94.23	106.19	36.0
65½	1.8125	162.5	88.65	113.05	95.13	107.54	31.2
66	1.8182	163.6	89.55	113.40	96.10	108.97	24.5
65¼	1.8239	164.8	90.60	113.76	97.22	110.60	15.0
65½	1.8297	165.9	91.80	114.12	98.51	112.42	+2.5
66	1.8354	167.1	93.19	114.47	100.00	114.47	-21.0

## ALLOWANCE FOR TEMPERATURE

At 10°Bé. .029°Bé. or .00023 Sp. Gr. = 1°F. At 50°Bé. .028° Bé. or .00045 Sp. Gr. = 1°F.  
 At 20°Bé. .036°Bé. or .00034 Sp. Gr. = 1°F. At 60°Bé. .026° Bé. or .00053 Sp. Gr. = 1°F.  
 At 30°Bé. .035°Bé. or .00039 Sp. Gr. = 1°F. At 63°Bé. .026° Bé. or .00057 Sp. Gr. = 1°F.  
 At 40°Bé. .031°Bé. or .00041 Sp. Gr. = 1°F. At 66°Bé. .0235°Bé. or .00054 Sp. Gr. = 1°F.

Specific gravity, 60°F. compared to H<sub>2</sub>O at 60°F. Oil of Vitriol = O.V. = 66°Bé. Freezing pts. based on Gable, Betz, & Maron, J. Am. Chem. Soc., 72, 1445, 1960; rest of table adopted as standard, 1904, Manufacturing Chemists' Assoc. of U. S. (authorities, Ferguson & Talbot).

## SULFURIC ACID, 94-100%

% w/w H <sub>2</sub> SO <sub>4</sub>	sp. gr. 60/60°F.	lbs. per cu. ft.	% w/w O.V.	lbs. O.V. per cu. ft.	Freezing pt., °F.	% w/w SO <sub>3</sub>	lbs. SO <sub>3</sub> per cu. ft.
94.0	1.8381	114.64	100.87	115.64	-28.0	76.73	87.97
95.0	1.8407	114.80	101.94	117.03	-8.0	77.55	89.03
96.0	1.8427	114.93	103.01	118.39	+7.0	78.37	90.07
97.0	1.8437	114.99	104.09	119.69	19.5	79.18	91.05
97.5	1.8439	115.00	104.63	120.32	(24)	79.59	91.53
98.0	1.8437	114.99	105.16	120.92	30.0	80.00	91.99
99.0	1.8424	114.91	106.23	122.07	41.0	80.82	92.87
100.0	1.8391	114.70	107.31	123.08	51.7	81.63	93.63

## ALLOWANCE FOR TEMPERATURE

At 94%, .00054 Sp. Gr. = 1°F.

At 97.5%, .00052 Sp. Gr. = 1°F.

At 96%, .00053 Sp. Gr. = 1°F.

At 100%, .00052 Sp. Gr. = 1°F.

Specific gravity, 60°F. compared to water at 60°F. Oil of Vitriol = O.V. = 66° Bé.  
Freezing points based on Gable, Betz, & Maron, J. Am. Chem. Soc., 72, 1445, 1960;  
rest of table adopted as standard, 1938, Manufacturing Chemists' Assoc. of U. S. (author-  
ity, Bishop).

## APPROXIMATE BOILING POINTS OF SULFURIC ACID \*

degrees Baumé	boiling pt., °F.	degrees Baumé	boiling pt., °F.	% w/w H <sub>2</sub> SO <sub>4</sub>	boiling pt., °F.
15	217	60	380	94	548
30	230	61	393	95	566
45	267	62	408	96	586
50	292	63	426	97	606
54	318	64	447	98	621
56	335	65	477	99	590
58	355	66	535	100	526

\* Values based on analysis of modern data, staff, Allied Chem. Corp.

## FUMING SULFURIC ACID EQUIVALENTS

Total SO <sub>2</sub>	Equivalent H <sub>2</sub> SO <sub>4</sub>	Per Cent H <sub>2</sub> SO <sub>4</sub>	Per Cent Free SO <sub>2</sub>	Total SO <sub>2</sub>	Equivalent H <sub>2</sub> SO <sub>4</sub>	Per Cent H <sub>2</sub> SO <sub>4</sub>	Per Cent Free SO <sub>2</sub>
81 63	100.00	100	0	90.82	111.25	50	50
81 82	100 23	99	1	91.00	111.48	49	51
82 00	100 45	98	2	91.18	111.70	48	52
82 18	100 67	97	3	91.37	111.93	47	53
82 37	100 90	96	4	91.55	112.15	46	54
82 55	101.13	95	5	91.73	112.37	45	55
82.73	101.35	94	6	91.92	112.60	44	56
82 92	101 58	93	7	92.10	112.82	43	57
83 10	101.80	92	8	92.29	113.05	42	58
83.29	102.03	91	9	92.47	113.28	41	59
83 47	102.25	90	10	92.65	113.50	40	60
83 65	102.47	89	11	92 84	113.73	39	61
83 84	102.70	88	12	93.02	113.95	38	62
84 02	102 92	87	13	93.20	114.17	37	63
84 20	103.15	86	14	93.39	114.40	36	64
84 39	103.38	85	15	93.57	114.62	35	65
84 57	103.60	84	16	93 76	114.85	34	66
84 75	103 82	83	17	93.94	115.08	33	67
84 94	104 05	82	18	94.12	115.30	32	68
85 12	104 27	81	19	94.31	115 53	31	69
85 31	104 50	80	20	94 49	115.75	30	70
85 49	104.73	79	21	94 67	115.97	29	71
85 67	104 95	78	22	94 86	116.20	28	72
85 86	105.18	77	23	95 04	116.42	27	73
86 04	105 40	76	24	95 22	116.65	26	74
86 22	105 62	75	25	95 41	116.88	25	75
86 41	105 85	74	26	95 59	117 10	24	76
86 59	106 07	73	27	95 78	117.33	23	77
86 78	106 30	72	28	95 96	117.55	22	78
86 96	106 53	71	29	96 14	117.77	21	79
87.14	106 75	70	30	96 33	118.00	20	80
87 33	106 98	69	31	96 51	118.22	19	81
87 51	107 20	68	32	96.69	118.45	18	82
87 69	107.42	67	33	96 88	118 68	17	83
87 88	107 65	66	34	97.06	118.90	16	84
88 06	107.87	65	35	97.25	119.13	15	85
88 24	108 10	64	36	97.43	119.35	14	86
88 43	108.33	63	37	97.61	119.57	13	87
88.61	108.55	62	38	97 80	119.80	12	88
88 80	108 78	61	39	97.98	120.03	11	89
88 98	109 00	60	40	98.16	120.25	10	90
89 16	109 22	59	41	98.35	120.48	9	91
89 35	109.45	58	42	98.53	120.70	8	92
89 53	109.67	57	43	98.71	120.92	7	93
89.71	109.90	56	44	98.90	121.15	6	94
89 90	110.13	55	45	99.08	121.37	5	95
90 08	110.35	54	46	99.27	121.60	4	96
90.27	110.58	53	47	99.45	121.83	3	97
90.45	110.80	52	48	99.63	122.05	2	98
90.63	111.02	51	49	99.82	122.28	1	99
				100.00	122.50	0	100

Compiled from the table by H. B. Bishop, Van Nostrand's Chemical Annual, 1913.

## NITRIC ACID

Degrees Baumé.	Sp. Gr. 60° F.	Degrees Twaddell.	Per Cent HNO <sub>3</sub> .	Degrees Baumé.	Sp. Gr. 60° F.	Degrees Twaddell.	Per Cent HNO <sub>3</sub> .
10.00	1.0741	14.82	12.86	21.25	1.1718	34.36	28.02
10.25	1.0761	15.22	13.18	21.50	1.1741	34.82	28.36
10.50	1.0781	15.62	13.49	21.75	1.1765	35.30	28.72
10.75	1.0801	16.02	13.81	22.00	1.1789	35.78	29.07
11.00	1.0821	16.42	14.13	22.25	1.1813	36.26	29.43
11.25	1.0841	16.82	14.44	22.50	1.1837	36.74	29.78
11.50	1.0861	17.22	14.76	22.75	1.1861	37.22	30.14
11.75	1.0881	17.62	15.07	23.00	1.1885	37.70	30.49
12.00	1.0902	18.04	15.41	23.25	1.1910	38.20	30.86
12.25	1.0922	18.44	15.72	23.50	1.1934	38.68	31.21
12.50	1.0943	18.86	16.05	23.75	1.1959	39.18	31.58
12.75	1.0964	19.28	16.39	24.00	1.1983	39.66	31.94
13.00	1.0985	19.70	16.72	24.25	1.2008	40.16	32.31
13.25	1.1006	20.12	17.05	24.50	1.2033	40.66	32.68
13.50	1.1027	20.54	17.38	24.75	1.2058	41.16	33.05
13.75	1.1048	20.96	17.71	25.00	1.2083	41.66	33.42
14.00	1.1069	21.38	18.04	25.25	1.2109	42.18	33.80
14.25	1.1090	21.80	18.37	25.50	1.2134	42.68	34.17
14.50	1.1111	22.22	18.70	25.75	1.2160	43.20	34.56
14.75	1.1132	22.64	19.02	26.00	1.2185	43.70	34.94
15.00	1.1154	23.08	19.36	26.25	1.2211	44.22	35.33
15.25	1.1176	23.52	19.70	26.50	1.2236	44.72	35.70
15.50	1.1197	23.94	20.02	26.75	1.2262	45.24	36.09
15.75	1.1219	24.38	20.36	27.00	1.2288	45.76	36.48
16.00	1.1240	24.80	20.69	27.25	1.2314	46.28	36.87
16.25	1.1262	25.24	21.03	27.50	1.2340	46.80	37.26
16.50	1.1284	25.68	21.36	27.75	1.2367	47.34	37.67
16.75	1.1306	26.12	21.70	28.00	1.2393	47.86	38.06
17.00	1.1328	26.56	22.04	28.25	1.2420	48.40	38.46
17.25	1.1350	27.00	22.38	28.50	1.2446	48.92	38.85
17.50	1.1373	27.46	22.74	28.75	1.2473	49.46	39.25
17.75	1.1395	27.90	23.08	29.00	1.2500	50.00	39.66
18.00	1.1417	28.34	23.42	29.25	1.2527	50.54	40.06
18.25	1.1440	28.80	23.77	29.50	1.2554	51.08	40.47
18.50	1.1462	29.24	24.11	29.75	1.2582	51.64	40.89
18.75	1.1485	29.70	24.47	30.00	1.2609	52.18	41.30
19.00	1.1508	30.16	24.82	30.25	1.2637	52.74	41.72
19.25	1.1531	30.62	25.18	30.50	1.2664	53.28	42.14
19.50	1.1554	31.08	25.53	30.75	1.2692	53.84	42.58
19.75	1.1577	31.54	25.88	31.00	1.2719	54.38	43.00
20.00	1.1600	32.00	26.24	31.25	1.2747	54.94	43.44
20.25	1.1624	32.48	26.61	31.50	1.2775	55.50	43.89
20.50	1.1647	32.94	26.96	31.75	1.2804	56.08	44.34
20.75	1.1671	33.42	27.33	32.00	1.2832	56.64	44.78
21.00	1.1694	33.88	27.67	32.25	1.2861	57.22	45.24



## NITRIC ACID (Continued)

Degrees Baumé.	Sp. Gr. 60° F.	Degrees Twaddell.	Per Cent HNO <sub>3</sub> .	Degrees Baumé.	Sp. Gr. 60° F.	Degrees Twaddell.	Per Cent HNO <sub>3</sub> .
32.50	1.2889	57.78	45.68	40.75	1.3909	78.18	63.48
32.75	1.2918	58.36	46.14	41.00	1.3942	78.84	64.20
33.00	1.2946	58.92	46.58	41.25	1.3976	79.52	64.93
33.25	1.2975	59.50	47.04	41.50	1.4010	80.20	65.67
33.50	1.3004	60.08	47.49	41.75	1.4044	80.88	66.42
33.75	1.3034	60.68	47.95	42.00	1.4078	81.56	67.18
34.00	1.3063	61.26	48.42	42.25	1.4112	82.24	67.95
34.25	1.3093	61.86	48.90	42.50	1.4146	82.92	68.73
34.50	1.3122	62.44	49.35	42.75	1.4181	83.62	69.52
34.75	1.3152	63.04	49.83	43.00	1.4216	84.32	70.33
35.00	1.3182	63.64	50.32	43.25	1.4251	85.02	71.15
35.25	1.3212	64.24	50.81	43.50	1.4286	85.72	71.98
35.50	1.3242	64.84	51.30	43.75	1.4321	86.42	72.82
35.75	1.3273	65.46	51.80	44.00	1.4356	87.12	73.67
36.00	1.3303	66.06	52.30	44.25	1.4392	87.84	74.53
36.25	1.3334	66.68	52.81	44.50	1.4428	88.56	75.40
36.50	1.3364	67.28	53.32	44.75	1.4464	89.28	76.28
36.75	1.3395	67.90	53.84	45.00	1.4500	90.00	77.17
37.00	1.3426	68.52	54.36	45.25	1.4536	90.72	78.07
37.25	1.3457	69.14	54.89	45.50	1.4573	91.46	79.03
37.50	1.3488	69.76	55.43	45.75	1.4610	92.20	80.04
37.75	1.3520	70.40	55.97	46.00	1.4646	92.92	81.08
38.00	1.3551	71.02	56.52	46.25	1.4684	93.68	82.18
38.25	1.3583	71.66	57.08	46.50	1.4721	94.42	83.33
38.50	1.3615	72.30	57.65	46.75	1.4758	95.16	84.48
38.75	1.3647	72.94	58.23	47.00	1.4796	95.92	85.70
39.00	1.3679	73.58	58.82	47.25	1.4834	96.68	86.98
39.25	1.3712	74.24	59.43	47.50	1.4872	97.44	88.32
39.50	1.3744	74.88	60.06	47.75	1.4910	98.20	89.76
39.75	1.3777	75.54	60.71	48.00	1.4948	98.96	91.35
40.00	1.3810	76.20	61.38	48.25	1.4987	99.74	93.13
40.25	1.3843	76.86	62.07	48.50	1.5026	100.52	95.11
40.50	1.3876	77.52	62.77				

## ALLOWANCE FOR TEMPERATURE

From 10° to 20° Bé., correction of  $\frac{1}{30}$ ° Bé. or .00029 Sp. Gr. = 1°F.

From 20° to 30° Bé., correction of  $\frac{1}{23}$ ° Bé. or .00044 Sp. Gr. = 1°F.

From 30° to 40° Bé., correction of  $\frac{1}{20}$ ° Bé. or .00060 Sp. Gr. = 1°F.

From 40° to 48.5° Bé., correction of  $\frac{1}{17}$ ° Bé. or .00084 Sp. Gr. = 1°F.

Specific gravity, 60°F. compared to water at 60°F. Table adopted as standard, 1903, by the Manufacturing Chemists' Assoc. of U. S. (authority, Ferguson).

## NITRIC ACID

*After Lunge and Rey*

Sp. gr. 15°/4° C.	Per cent by weight		1 liter con- tains grams		Sp. gr. 15°/4° C.	Per cent by weight		1 liter con- tains grams	
	N <sub>2</sub> O <sub>5</sub>	HNO <sub>3</sub>	N <sub>2</sub> O <sub>5</sub>	HNO <sub>3</sub>		N <sub>2</sub> O <sub>5</sub>	HNO <sub>3</sub>	N <sub>2</sub> O <sub>5</sub>	HNO <sub>3</sub>
1.000	0.08	0.10	1	1	1.195	27.10	31.62	324	378
1.005	0.85	1.00	8	10	1.200	27.74	32.36	333	388
1.010	1.62	1.90	16	19	1.205	28.36	33.09	342	399
1.015	2.39	2.80	24	28	1.210	28.99	33.82	351	409
1.020	3.17	3.70	33	38	1.215	29.61	34.55	360	420
1.025	3.94	4.60	40	47	1.220	30.24	35.28	369	430
1.030	4.71	5.50	49	57	1.225	30.88	36.03	378	441
1.035	5.47	6.38	57	66	1.230	31.53	36.78	387	452
1.040	6.22	7.26	64	75	1.235	32.17	37.53	397	463
1.045	6.97	8.13	73	85	1.240	32.82	38.29	407	475
1.050	7.71	8.99	81	94	1.245	33.47	39.05	417	486
1.055	8.43	9.84	89	104	1.250	34.13	39.82	427	498
1.060	9.15	10.68	97	113	1.255	34.78	40.58	437	509
1.065	9.87	11.51	105	123	1.260	35.44	41.34	447	521
1.070	10.57	12.33	113	132	1.265	36.09	42.10	457	533
1.075	11.27	13.15	121	141	1.270	36.75	42.87	467	544
1.080	11.96	13.95	129	151	1.275	37.41	43.64	477	556
1.085	12.64	14.74	137	160	1.280	38.07	44.41	487	568
1.090	13.31	15.53	145	169	1.285	38.73	45.18	498	581
1.095	13.99	16.32	153	179	1.290	39.39	45.95	508	593
1.100	14.67	17.11	161	188	1.295	40.05	46.72	519	605
1.105	15.34	17.89	170	198	1.300	40.71	47.49	529	617
1.110	16.00	18.67	177	207	1.305	41.37	48.26	540	630
1.115	16.67	19.45	186	217	1.310	42.06	49.07	551	643
1.120	17.34	20.23	195	227	1.315	42.76	49.89	562	656
1.125	18.00	21.00	202	236	1.320	43.47	50.71	573	669
1.130	18.66	21.77	211	246	1.325	44.17	51.53	585	683
1.135	19.32	22.54	219	256	1.330	44.89	52.37	597	697
1.140	19.98	23.31	228	266	1.3325	45.26	52.80	603	704
1.145	20.64	24.08	237	276	1.335	45.62	53.22	609	710
1.150	21.29	24.84	245	286	1.340	46.35	54.07	621	725
1.155	21.94	25.60	254	296	1.345	47.08	54.93	633	739
1.160	22.60	26.36	262	306	1.350	47.82	55.79	645	753
1.165	23.25	27.12	271	316	1.355	48.57	56.66	658	768
1.170	23.90	27.88	279	326	1.360	49.35	57.57	671	783
1.175	24.54	28.63	288	336	1.365	50.13	58.48	684	798
1.180	25.18	29.38	297	347	1.370	50.91	59.39	698	814
1.185	25.83	30.13	306	357	1.375	51.69	60.30	711	829
1.190	26.47	30.88	315	367	1.380	52.52	61.27	725	846

## NITRIC ACID (Continued)

Sp. gr 15°/4° C.	Per cent by weight		1 liter con- tains grams		Sp. gr 15°/4° C.	Per cent by weight		1 liter con- tains grams	
	N <sub>2</sub> O <sub>5</sub>	HNO <sub>3</sub>	N <sub>2</sub> O <sub>5</sub>	HNO <sub>3</sub>		N <sub>2</sub> O <sub>5</sub>	HNO <sub>3</sub>	N <sub>2</sub> O <sub>5</sub>	HNO <sub>3</sub>
1.3833	53.08	61.92	735	857	1.495	78.52	91.60	1174	1369
1.385	53.35	62.24	739	862	1.500	80.65	94.09	1210	1411
1.390	54.20	63.23	753	879	1.501	81.09	94.60	1217	1420
1.395	55.07	64.25	768	896	1.502	81.50	95.08	1224	1428
1.400	55.97	65.30	783	914	1.503	81.91	95.55	1231	1436
1.405	56.92	66.40	800	933	1.504	82.29	96.00	1238	1444
1.410	57.86	67.50	816	952	1.505	82.63	96.39	1244	1451
1.415	58.83	68.63	832	971	1.506	82.94	96.76	1249	1457
1.420	59.83	69.80	849	991	1.507	83.26	97.13	1255	1464
1.425	60.84	70.98	867	1011	1.508	83.58	97.50	1260	1470
1.430	61.86	72.17	885	1032	1.509	83.87	97.84	1265	1476
1.435	62.91	73.39	903	1053	1.510	84.09	98.10	1270	1481
1.440	64.01	74.63	921	1075	1.511	84.28	98.32	1274	1486
1.445	65.13	75.98	941	1098	1.512	84.46	98.53	1277	1490
1.450	66.24	77.28	961	1121	1.513	84.63	98.73	1280	1494
1.455	67.38	78.60	981	1144	1.514	84.78	98.90	1283	1497
1.460	68.56	79.98	1001	1168	1.515	84.92	99.07	1287	1501
1.465	69.79	81.42	1023	1193	1.516	85.04	99.21	1289	1504
1.470	71.06	82.90	1045	1219	1.517	85.15	99.34	1292	1507
1.475	72.39	84.45	1068	1246	1.518	85.26	99.46	1294	1510
1.480	73.76	86.05	1092	1274	1.519	85.35	99.57	1296	1512
1.485	75.18	87.70	1116	1302	1.520	85.44	99.67	1299	1515
1.490	76.80	89.60	1144	1335					

For data on the density of nitric acid at temperatures other than 15°C., see International Critical Tables, 3, 58-9.

## COMPOSITION OF CONSTANT BOILING HYDROCHLORIC ACID \*

pressure in mm. of mercury	wt. of distil- late in grams in air to give 1 mole of HCl	pressure in mm. of mercury	wt. of distil- late in grams in air to give 1 mole of HCl
600	176.745	700	178.946
620	177.228	740	179.762
630	177.470	750	179.966
640	177.711	760	180.169
650	177.953	770	180.373
660	178.194	780	180.577
680	178.538		

\* Data from Williams, S., J. Assoc. Official Agr. Chemists, 37, 462, 1954.

## HYDROCHLORIC ACID

*After Lunge and Marchlewski*

Specific Gravity. 15° 4° In Vacuo.	Per Cent HCl by Weight.	1 Liter con- tains Grams HCl.	Specific Gravity 15° 4° in Vacuo.	Per Cent HCl by Weight.	1 Liter con- tains Grams HCl.	Specific Gravity 15° 4° in Vacuo.	Per Cent HCl by Weight.	1 Liter con- tains Grams HCl.
1.000	0.16	1.6	1.075	15.16	163	1.145	28.61	328
1.005	1.15	12	1.080	16.15	174	1.150	29.57	340
1.010	2.14	22	1.085	17.13	186	1.152	29.95	345
1.015	3.12	32	1.090	18.11	197	1.155	30.55	353
1.020	4.13	42	1.095	19.06	209	1.160	31.52	366
1.025	5.15	53	1.100	20.01	220	1.163	32.10	373
1.030	6.15	64	1.105	20.97	232	1.165	32.49	379
1.035	7.15	74	1.110	21.92	243	1.170	33.46	392
1.040	8.16	85	1.115	22.86	255	1.171	33.65	394
1.045	9.16	96	1.120	23.82	267	1.175	34.42	404
1.050	10.17	107	1.125	24.78	278	1.180	35.39	418
1.055	11.18	118	1.130	25.75	291	1.185	36.31	430
1.060	12.19	129	1.135	26.70	303	1.190	37.23	443
1.065	13.19	141	1.140	27.66	315	1.195	38.16	456
1.070	14.17	152	1.1425	28.14	322	1.200	39.11	469

For data on the density of hydrochloric acid at temperatures other than 15°C., see International Critical Tables, 3, 54.

## ACETIC ACID \*

% w/w acetic acid	specific gravity 20°/4°C.	% w/w acetic acid	specific gravity 20°/4°C.	% w/w acetic acid	specific gravity 20°/4°C.	% w/w acetic acid	specific gravity 20°/4°C.
0	0.9982	26	1.0338	52	1.0590	78	1.0700
2	1.0012	28	1.0361	54	1.0604	80	1.0700
4	1.0040	30	1.0384	56	1.0618	82	1.0698
6	1.0069	32	1.0406	58	1.0631	84	1.0693
8	1.0097	34	1.0428	60	1.0642	86	1.0685
10	1.0125	36	1.0449	62	1.0653	88	1.0675
12	1.0154	38	1.0469	64	1.0662	90	1.0661
14	1.0182	40	1.0488	66	1.0671	92	1.0643
16	1.0209	42	1.0507	68	1.0678	94	1.0619
18	1.0236	44	1.0525	70	1.0685	96	1.0588
20	1.0263	46	1.0542	72	1.0690	98	1.0549
22	1.0288	48	1.0559	74	1.0694	99	1.0524
24	1.0313	50	1.0575	76	1.0698	100	1.0498

\* Selected values, International Critical Tables, 3, 123-124; q.v. for specific gravities at other temperatures.

PHOSPHORIC ACID, 20-110% \*

$\% w/w$ $H_3PO_4$	sp. gr. 25°/15.5° C.	$\% w/w$ $H_3PO_4$	sp. gr. 25°/15.5° C.	$\% w/w$ $H_3PO_4$	sp. gr. 25°/15.5° C.
20.0	1.1143	70.1	1.523	84.0	1.6745
21.0	1.1207	70.3	1.525	84.2	1.677
22.0	1.1271	70.5	1.527	84.4	1.679
23.0	1.1336	71.0	1.5320	84.6	1.681
24.0	1.1400	72.0	1.5424	84.8	1.684
25.0	1.1467	73.0	1.5529	85.0	1.6861
26.0	1.1534	74.0	1.5635	85.2	1.688
27.0	1.1601	74.5	1.569	85.4	1.691
28.0	1.1669	74.7	1.571	85.6	1.693
29.0	1.1738	75.0	1.5742	85.8	1.695
30.0	1.1807	75.2	1.576	86.0	1.6977
31.0	1.1877	75.4	1.578	86.5	1.704
32.0	1.1948	75.6	1.581	87.0	1.7095
33.0	1.2019	75.8	1.583	87.5	1.716
34.0	1.2092	76.0	1.5849	88.0	1.7214
35.0	1.2164	76.2	1.587	88.5	1.727
36.0	1.2238	76.4	1.589	89.0	1.7334
37.0	1.2312	76.6	1.591	89.5	1.739
38.0	1.2387	76.8	1.594	90.0	1.7455
39.0	1.2462	77.0	1.5958	91.0	1.7578
40.0	1.2539	77.2	1.598	92.0	1.7685
41.0	1.2616	77.4	1.600	93.0	1.7813
42.0	1.2694	77.6	1.602	94.0	1.7937
43.0	1.2772	77.8	1.605	95.0	1.8062
44.0	1.2852	78.0	1.6067	96.0	1.8186
45.0	1.2932	78.2	1.609	97.0	1.8311
46.0	1.3014	78.4	1.611	98.0	1.8436
47.0	1.3096	78.6	1.613	99.0	1.8560
48.0	1.3178	78.8	1.616	100.0	1.8686
49.0	1.3263	79.0	1.6178	101.0	1.8810
50.0	1.3347	79.2	1.620	102.0	1.8935
51.0	1.3432	79.4	1.622	103.0	1.9060
52.0	1.3518	79.6	1.625	103.5	1.912
53.0	1.3605	79.8	1.627	103.7	1.915
54.0	1.3692	80.0	1.6290	104.0	1.9184
55.0	1.3781	80.2	1.631	104.2	1.921
56.0	1.3870	80.4	1.634	104.4	1.923
57.0	1.3960	80.6	1.636	104.6	1.926
58.0	1.4051	80.8	1.638	104.8	1.928
59.0	1.4143	81.0	1.6403	105.0	1.9309
60.0	1.4236	81.2	1.643	105.2	1.933
61.0	1.4330	81.4	1.645	105.4	1.936
62.0	1.4425	81.6	1.647	105.6	1.938
63.0	1.4520	81.8	1.649	105.8	1.941
64.0	1.4617	82.0	1.6516	106.0	1.9433
65.0	1.4714	82.2	1.654	106.2	1.946
66.0	1.4813	82.4	1.656	106.4	1.948
67.0	1.4912	82.6	1.658	106.5	1.950
68.0	1.5013	82.8	1.661	107.0	1.9558
69.0	1.5114	83.0	1.6630	108.0	1.9684
69.5	1.517	83.2	1.665	109.0	1.9808
69.6	1.518	83.4	1.668	110.0	1.9933
69.8	1.520	83.6	1.670		
70.0	1.5216	83.8	1.672		

ALLOWANCE FOR TEMPERATURE IN THE RANGE 21-29°C.

The following corrections are subtracted for each degree Centigrade below 25°C. and added for each degree above 25°C.

$\% w/w$ $H_3PO_4$	Allowance	$\% w/w$ $H_3PO_4$	Allowance	$\% w/w$ $H_3PO_4$	Allowance
20	.00038	45	.00058	70	.00073
25	.00042	50	.00059	75	.00075
30	.00045	55	.00062	80	.00077
35	.00050	60	.00064	85	.00078
40	.00056	65	.00068	90	.00080

\* Based on data of Christensen, J. H. and Reed, R. B., *Ind. Eng. Chem.*, **47**, 1277, 1950; Egan, E. P., Jr., and Luff, B. B., *ibid.*, **47**, 1280, 1950; 92-110%  $H_3PO_4$  data, staff, Monsanto Chem. Co. in part unpublished.

## AQUA AMMONIA, 25.5-31.4% \*

°Bé, 60°F.	% w/w NH <sub>3</sub>	°Bé, 60°F.	% w/w NH <sub>3</sub>	°Bé, 60°F.	% w/w NH <sub>3</sub>	°Bé, 60°F.	% w/w NH <sub>3</sub>
24.00	25.48	24.80	27.05	25.60	28.62	26.40	30.18
24.10	25.68	24.90	27.24	25.70	28.81	26.50	30.38
24.20	25.87	25.00	27.44	25.80	29.01	26.60	30.58
24.30	26.07	25.10	27.64	25.90	29.20	26.70	30.77
24.40	26.26	25.20	27.83	26.00	29.40	26.80	30.97
24.50	26.46	25.30	28.03	26.10	29.60	26.90	31.16
24.60	26.66	25.40	28.22	26.20	29.79	27.00	31.36
24.70	26.85	25.50	28.42	26.30	29.99		

## ALLOWANCE FOR TEMPERATURE \*

(To be added for each degree below 60°F.)

°Bé read	Temperature, °F.					
	40°	42°	44°	46°	48°	50°
24.0	0.046	0.047	0.047	0.048	0.049	0.050
24.2	0.047	0.047	0.048	0.049	0.049	0.050
24.4	0.047	0.048	0.049	0.049	0.050	0.051
24.6	0.048	0.049	0.049	0.050	0.051	0.052
24.8	0.049	0.049	0.050	0.051	0.052	0.053
25.0	0.050	0.050	0.051	0.052	0.052	0.053
25.2	0.050	0.051	0.052	0.052	0.053	0.054
25.4	0.051	0.052	0.052	0.053	0.054	0.055
25.6	0.052	0.052	0.053	0.054	0.055	0.055
25.8	0.052	0.053	0.054	0.054	0.055	0.056
26.0	0.053	0.054	0.054	0.055	0.056	0.057

\* Calculated by staff, E. I. DuPont de Nemours &amp; Co., Inc.

## AQUA AMMONIA \*

Degrees Baumé.	Sp. Gr. 60° F.	Per Cent NH <sub>3</sub> .	Degrees Baumé.	Sp. Gr. 60° F.	Per Cent NH <sub>3</sub> .	Degrees Baumé.	Sp. Gr. 60° F.	Per Cent NH <sub>3</sub> .
10.00	1.0000	.00	16.50	.9556	11.18	23.00	.9150	23.52
10.25	.9982	.40	16.75	.9540	11.64	23.25	.9135	24.01
10.50	.9964	.80	17.00	.9524	12.10	23.50	.9121	24.50
10.75	.9947	1.21	17.25	.9508	12.56	23.75	.9106	24.99
11.00	.9929	1.62	17.50	.9492	13.02	24.00	.9091	25.48
11.25	.9912	2.04	17.75	.9475	13.49	24.25	.9076	25.97
11.50	.9894	2.46	18.00	.9459	13.96	24.50	.9061	26.46
11.75	.9876	2.88	18.25	.9444	14.43	24.75	.9047	26.95
12.00	.9859	3.30	18.50	.9428	14.90	25.00	.9032	27.44
12.25	.9842	3.73	18.75	.9412	15.37	25.25	.9018	27.93
12.50	.9825	4.16	19.00	.9396	15.84	25.50	.9003	28.42
12.75	.9807	4.59	19.25	.9380	16.32	25.75	.8989	28.91
13.00	.9790	5.02	19.50	.9365	16.80	26.00	.8974	29.40
13.25	.9773	5.45	19.75	.9349	17.28	26.25	.8960	29.89
13.50	.9756	5.88	20.00	.9333	17.76	26.50	.8946	30.38
13.75	.9739	6.31	20.25	.9318	18.24	26.75	.8931	30.87
14.00	.9722	6.74	20.50	.9302	18.72	27.00	.8917	31.36
14.25	.9705	7.17	20.75	.9287	19.20	27.25	.8903	31.85
14.50	.9689	7.61	21.00	.9272	19.68	27.50	.8889	32.34
14.75	.9672	8.05	21.25	.9256	20.16	27.75	.8875	32.83
15.00	.9655	8.49	21.50	.9241	20.64	28.00	.8861	33.32
15.25	.9639	8.93	21.75	.9226	21.12	28.25	.8847	33.81
15.50	.9622	9.38	22.00	.9211	21.60	28.50	.8833	34.30
15.75	.9605	9.83	22.25	.9195	22.08	28.75	.8819	34.79
16.00	.9589	10.28	22.50	.9180	22.56	29.00	.8805	35.28
16.25	.9573	10.73	22.75	.9165	23.04			

## ALLOWANCE FOR TEMPERATURE

The coefficient of expansion for ammonia solutions, varying with the temperature, correction must be applied according to the following table:

Corrections to be Added for Each Degree Below 60° F.			Corrections to be Subtracted for Each Degree Above 60° F.			
Degrees Baumé.	40° F.	50° F.	70° F.	80° F.	90° F.	100° F.
14° Bé	.015° Bé	.017° Bé	.020° Bé	.022° Bé	.024° Bé	.026° Bé
16°	.021 "	.023 "	.026 "	.028 "	.030 "	.032 "
18°	.027 "	.029 "	.031 "	.033 "	.035 "	.037 "
20°	.033 "	.036 "	.037 "	.038 "	.040 "	.042 "
22°	.039 "	.042 "	.043 "	.045 "	.047 "	
26°	.053 "	.057 "	.057 "	.059 "		

\* Values for Degrees Baumé, Light. Table adopted as official, 1903, Manufacturing Chemists' Assoc. of U. S. (authority Ferguson).

## SODIUM HYDROXIDE SOLUTIONS, 1-53% NaOH

% w/w		°Bé, 60°F.	sp. gr. 60/60°F.	% w/w		°Bé, 60°F.	sp. gr. 60/60°F.
NaOH	Na <sub>2</sub> O			NaOH	Na <sub>2</sub> O		
1.00	0.77	1.66	1.012	28.00	21.69	34.35	1.310
2.00	1.55	3.23	1.023	29.00	22.47	35.25	1.321
3.00	2.32	4.77	1.034	30.00	23.24	36.13	1.332
4.00	3.10	6.27	1.045	31.00	24.02	36.99	1.342
5.00	3.87	7.73	1.056	32.00	24.79	37.83	1.353
6.00	4.65	9.16	1.067	33.00	25.57	38.65	1.363
7.00	5.42	10.56	1.079	34.00	26.34	39.45	1.374
8.00	6.20	11.93	1.089	35.00	27.12	40.24	1.384
9.00	6.97	13.29	1.101	36.00	27.89	41.01	1.394
10.00	7.75	14.60	1.112	37.00	28.67	41.76	1.404
11.00	8.52	15.89	1.123	38.00	29.44	42.50	1.415
12.00	9.30	17.15	1.134	39.00	30.22	43.21	1.425
13.00	10.07	18.39	1.145	40.00	30.99	43.92	1.435
14.00	10.85	19.61	1.156	41.00	31.77	44.60	1.444
15.00	11.62	20.80	1.167	42.00	32.54	45.28	1.454
16.00	12.40	21.96	1.178	43.00	33.32	45.93	1.464
17.00	13.17	23.11	1.190	44.00	34.09	46.57	1.473
18.00	13.95	24.23	1.201	45.00	34.87	47.20	1.483
19.00	14.72	25.33	1.212	46.00	35.64	47.83	1.492
20.00	15.50	26.41	1.223	47.00	36.42	48.44	1.502
21.00	16.27	27.47	1.234	48.00	37.19	49.05	1.511
22.00	17.05	28.51	1.245	49.00	37.97	49.65	1.521
23.00	17.82	29.53	1.256	50.00	38.74	50.23	1.530
24.00	18.60	30.53	1.267	51.00	39.52	50.82	1.540
25.00	19.37	31.51	1.278	52.00	40.29	51.39	1.549
26.00	20.14	32.47	1.289	53.00	41.06	51.95	1.558
27.00	20.92	33.42	1.300				



## SODIUM HYDROXIDE SOLUTIONS, 4-50% NaOH

% w/w NaOH	Specific Gravity			% w/w NaOH	Specific Gravity		
	15°C.	20°C.	30°C.		15°C.	20°C.	30°C.
4	1.0444	1.0428	1.0393	28	1.3094	1.3064	1.3002
6	1.0667	1.0648	1.0609	30	1.3309	1.3279	1.3217
8	1.0889	1.0869	1.0826	32	1.3520	1.3490	1.3427
10	1.1111	1.1089	1.1043	34	1.3728	1.3696	1.3632
12	1.1333	1.1309	1.1261	36	1.3933	1.3900	1.3835
14	1.1554	1.1530	1.1480	38	1.4135	1.4101	1.4035
16	1.1776	1.1751	1.1699	40	1.4334	1.4300	1.4232
18	1.1997	1.1972	1.1918	42	1.4529	1.4494	1.4425
20	1.2218	1.2191	1.2136	44	1.4720	1.4685	1.4615
22	1.2439	1.2411	1.2454	46	1.4911	1.4873	1.4805
24	1.2658	1.2629	1.2571	48	1.5102	1.5065	1.4994
26	1.2877	1.2848	1.2789	50	1.5290	1.5253	1.5181

Specific gravity at stated temperature compared to water at 4°C.; selected values, International Critical Tables, 3, 79.

## Chapter 23

# AIR POLLUTANTS

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*Introduction.*—It is necessary to analyze both the air and effluents and emissions to the air in order to know: the kind and amount of pollution in a given place; how serious the air contamination is in a given community; whether the pollution of a community is increasing, decreasing, or remaining at the same level; whether the pollution concentration is high enough to sound an alert and warn the public of danger; how efficient the methods and equipment for control are; what concentration standards to set in order to control pollution; when a violation of those standards exists; and how successful research and development in the air pollution field really is. The sampling and analysis of air pollutants, for air pollution control, may be placed into seven analytical categories: (1) settled particulate matter; (2) suspended particulate matter; (3) gaseous, vapor, and aerosol contaminants; (4) stack emissions; (5) exhaust gases; (6) pollution source detection; and (7) radiochemical analysis. A discussion of the last four categories is beyond the scope of this chapter.

Scarcely a decade ago virtually the only analyses performed in this field were determination of sootfall (settled particulate matter) and sulfur dioxide. Within the decade the analysis of air pollutants had developed to such an extent that several books have been devoted to the topic.<sup>1</sup>

<sup>1</sup> Jacobs, Morris B., *The Chemical Analysis of Air Pollutants*, Interscience Publishers, Inc., New York, 1960; *Laboratory Methods*, Air Pollution Control District, Los Angeles County, California, 1958; *Methods of Atmospheric Sampling and Analysis*, ASTM Standards, Part 10, American Society for Testing Materials, Philadelphia, 1958; *Air Pollution Manual*, Am. Ind. Hyg. Assoc., Detroit, 1960.

# SETTLED PARTICULATE MATTER

The analysis for settled particulate matter from the air is also known as sootfall, dustfall, and particle-fall analysis. Widemouth, open top vessels containing water are exposed in a suitable location for a period, usually of one month. After this time the vessels are collected, properly covered, returned to the laboratory, and the contents are analyzed.

**Sampling. Collectors.**—Until 1959–1960, the principal collection vessels were 1-gal., widemouthed, glass jars, having a mouth diameter of 4.4 inches. Open top, straight wall, cylindrical vessels having a diameter of 6 inches and a height of 12 inches are now considered best. They must be capable of being closed with covers that do not leak, so that they may be transported to the laboratory without loss. They may be made of glass, plastic, or stainless steel.

**Sampling Sites.**—The sampling sites should be selected so that they are representative of the area being sampled. The collectors should be placed in holders so that the mouth of the collector vessel will be about 3 inches above the top of the holder. The collector vessel should be 4 feet above the roof or other platform on which it is placed, and it should be located in such a manner that it is not influenced by chimneys, walls, parapets, or other interfering structures. The roofs of 4-story buildings are generally best, and, where possible, public buildings such as schools should be used, as access to these may be better.

**Method.**—Place 1.5 to 2 l. of distilled water into the collectors. In the winter-time include sufficient antifreeze, such as isopropyl alcohol, to prevent freezing; in the summertime include a fungicide or algacide. Cover tightly, transport to the sampling site, place in position, and remove the cover. Leave exposed for 1 month. If possible, observe the collection vessel from time to time during the month to see that it contains sufficient collection fluid. At the end of the exposure period, return to the sampling site, cover the collector, replace it with another collector, and return the sample to the laboratory.

**Determination. Insoluble Solids.**—Transfer the contents of the collector vessel through a 20-mesh sieve to remove leaves, twigs, paper, and other extraneous matter that cannot be considered sootfall or dustfall, to a graduated cylinder of adequate volume, and read the volume of the collection fluid. Filter the contents of each collector through a tared, dry, filter paper, such as 9-cm. Whatman No. 41-H, to separate the insoluble matter from the soluble solids. Prepared Gooch crucibles or alundum crucibles may also be used. Save the filtrate for the estimation of soluble solids. Replace the filter paper in its weighing bottle and dry at 105°C. to constant weight; place in a desiccator to cool, and weigh. The weight of the additional material is the insoluble solids.

**Tar.**—Insert the weighed filter into a thimble of a Soxhlet extractor, and extract with carbon disulfide. After extraction is complete, remove the paper, replace in its drying bottle, dry, and reweigh. The loss in weight is considered to be tar.

**Insoluble Ash.**—After the determination of insoluble solids, or after the tar determination, place the filter into a tared crucible and heat until a char is formed.

Place the crucible in a muffle furnace, ignite, and burn to a clean ash at 500 to 600°C. Cool in a desiccator and weigh. The weight of the residue is the insoluble ash.

**Soluble Solids.**—Make up the filtrate from the insoluble solids' determination to a known volume. Transfer a suitable aliquot to a weighed dish, evaporate nearly to dryness on a steam bath, transfer to an oven, and dry at 105°C. Cool in a desiccator and weigh. The gain in weight, multiplied by the factor of the aliquot, yields the weight of the soluble solids in the sample.

**Soluble Ash.**—Ignite the residue in the dish in a muffle furnace at 500 to 600°C., and burn to a clean ash. Remove from the furnace, allow to cool, place in a desiccator, and weigh again. The gain in weight over the tared dish, multiplied by the factor for the aliquot taken, is the soluble solids ash.

**Calculations.**—The total settled particulate matter, or total sootfall, is computed by adding the insoluble solids and soluble solids. Total ash is computed by adding the insoluble solids ash and the soluble solids ash. To express the results in terms of tons per square mile per month, the usual form of expression, the following equation may be used:

$$X = 5650 \frac{w}{D^2}$$

where  $X$  = sootfall or other contaminant in tons per square mile,

$w$  = weight of the solids or other material or substance in g.,

and  $D$  = diameter of the collector in inches.

Since it is difficult to arrange to pick up the collectors exactly at the end of each 30-day period, a factor must be used in the computation to adjust for the length of exposure time. It is best, however, not to exceed plus or minus 2 days. The factors for monthly basis calculations are: 28 days, 0.334; 29, 0.323; 30, 0.312; 31, 0.302; 32, 0.293. These factors are used to convert milligrams of sootfall to tons per square mile, and are based on a collector having a mouth diameter of  $4\frac{5}{16}$  inches. Methods for dustfall have been adopted by the Air Measurements Committee of the Air Pollution Control Association,<sup>2</sup> the D-22 Committee of the American Society for Testing and Materials,<sup>3</sup> and by the Air Pollution Control District of Los Angeles County.<sup>4</sup> The determination of settled particulate matter has been carried on in Great Britain for many years.<sup>5</sup>

<sup>2</sup> Committee on Air Pollution Measurements, APCA, H. M. Chapman, Chairman, J. Air Pollution Control Assoc., 5, No. 3, 176, 1955.

<sup>3</sup> Method for Collection and Analysis of Dustfall, Designation: D1739-60T, ASTM Standards, Part 10, American Society for Testing and Materials, Philadelphia, 1585, 1961.

<sup>4</sup> Laboratory Method, Air Pollution Control District, Los Angeles County, California, 1958.

<sup>5</sup> The Investigation of Atmospheric Pollution, Dept. Sci. Ind. Research, Fuel Research, London, 1952; Jacobs, Morris B., The Chemical Analysis of Air Pollutants, Interscience Publishers, Inc., New York, 1960.

# SUSPENDED PARTICULATE MATTER

To determine total suspended particulate matter, air is passed through a tared filter, which has been dried and weighed, at a known rate for a known period of time. The filter is then redried and reweighed. The gain in weight divided by the volume of computed air gives the total suspended particulate matter in units of weight per volume, generally micrograms per cubic meter. Of the various types of filters used, the most common is the glass filter web<sup>6</sup> adopted by the Public Health Service Sanitary Engineering Center. These are 8 × 10 inch sheets weighing approximately 4 g. The high volume samplers used are modifications of the one developed by Silverman and Viles.<sup>7</sup> These, as well as stands for holding the sampler, and rotameters for measuring the volume of air drawn through the filter, are available commercially.

**Sampling.**—After drying the glass fiber web, and obtaining its weight to the nearest mg., put it in an envelope, transport it to the sampling place, and place it carefully in the holder of the high volume sampler. Replace the sampler in its housing, with the filter paper facing up, and turn on the motor. Note the rotameter reading, that is, the initial sampling rate, the time, and the weather conditions. Return to the sampling place as close to 24 hours later as possible, and again note the rotameter reading, the time, and the weather conditions. Stop the motor, take out the filter, fold it once along the long axis, put it in its envelope and return to the laboratory.

**Determination.**—Dry the filter in an oven overnight at 100° to 105°C., allow it to cool, and reweigh to the nearest mg. The increase in weight is deemed the total suspended particulate matter.

**Calculation.**—The high volume sampler and its rotameter should be calibrated against a total gas volume instrument. Assuming that the increase in resistance is a straight line function of the clogging of the pores of the filter, obtain the average velocity of the air sampled by adding the initial and final velocities, that is, the rotameter readings, and dividing by two. Multiply by the number of minutes to get the total volume of air sampled. Multiply by the calibration factor. To express the results in milligrams per cubic meter:

$$\text{mg./cu. meter} = \frac{\text{mg.}}{V \times 0.02832}$$

where mg. = weight of the deposit in milligrams,  
and  $V$  = corrected volume of air sampled in cubic feet.

The suspended particulate matter can then be analyzed by methods developed and exploited by the National Air Sampling Network of the Public Health Service, Department of Health, Education, and Welfare.<sup>8</sup>

<sup>6</sup> Catalog No. CT-25310, also MSA No. 1106B, Mines Safety Appliances Co., Pittsburgh, Pa.

<sup>7</sup> Silverman, L., and Viles, F. J., *J. Ind. Hyg. Toxicol.*, 30, 124, 1948.

<sup>8</sup> Air Pollution Measurements of the National Air Sampling Network of Suspended Particulate Matter, 1953-1957, Public Health Serv., Publication 637, 1959.

# GASEOUS, VAPOR, AND AEROSOL CONTAMINANTS

The gaseous, vapor, and aerosol pollutants of the atmosphere can be placed into two major groups: (a) inorganic; and (b) organic. Here the term "aerosol" is used to designate such air contaminants as sulfur trioxide, sulfuric acid aerosol, chlorides, fluorides, and other salts in contrast to the nonspecific aerosols that comprise the suspended particulate matter.

## INORGANIC POLLUTANTS

The inorganic contaminants include: true gases such as sulfur dioxide, hydrogen sulfide, and carbon monoxide; the group of nitrogen oxides, ammonia, ozone, and oxidants; sulfur trioxide; and sulfuric acid aerosol. Other components, which are occasionally present, and then usually only in industrial atmospheres, are chlorine, fluorides, cyanides, and phosgene. Methods for the determination of the latter group, detailed elsewhere in the text, can be applied, with but little modification, to determining their presence in air.

### SULFUR DIOXIDE

The methods commonly used for the determination of sulfur dioxide in air are (a) the West and Gaeke<sup>9</sup> disulfitomercurate method and the peroxide method.

#### WEST AND GAEKE METHOD

Sulfur dioxide is removed from the air being sampled by scrubbing through 0.1 *M* sodium tetrachloromercurate(II), forming stable nonvolatile disulfitomercurate(II). The amount of sulfur dioxide trapped is determined by the red-violet color obtained with pararosaniline hydrochloride-hydrochloric acid mixture and formaldehyde. The absorption maximum of the complex is 560  $m\mu$ . The color is not affected by temperature, and is stable for several hours.

**Reagents.** **Sodium Tetrachloromercurate(II) Solution (0.1 *M*).**—Dissolve 27.2 g. (0.1 mole) of reagent grade mercuric chloride and 11.7 g. (0.2 mole) of reagent grade sodium chloride in water and dilute to 1 liter.

**Hydrochloric Acid Bleached Pararosaniline Solution.**—Mix 4 ml. of 0.25% aqueous solution of pararosaniline hydrochloride and 6 ml. of concentrated hydrochloric acid and dilute to 100 ml. Only dyes with absorption maxima at 543 or 544  $m\mu$  should be used. Those having absorption maxima at 549 or 550 should be rejected.<sup>9a</sup>

**Formaldehyde Solution (0.2%).**—Dilute 5 ml. of 40% formaldehyde solution to 1 liter with water.

<sup>9</sup> West, P. W., and Gaeke, G. C., *Anal. Chem.*, **28**, 1816, 1956.

<sup>9a</sup> Pate, John, *Anal. Chem.*, in press, 1962.

# SUSPENDED PARTICULATE

To determine total suspended particulate matter, air is passed through a filter, which has been dried and weighed, at a known rate for a known time. The filter is then redried and reweighed. The gain in weight divided by the volume of computed air gives the total suspended particulate weight per volume, generally micrograms per cubic meter. One of the types of filters used, the most common is the glass fiber web<sup>6</sup> and the high volume sampler used are one developed by Silverman and Viles.<sup>7</sup> These, as well as the high volume sampler, and rotameters for measuring the volume of air drawn are available commercially.

**Sampling.**—After drying the glass fiber web, and obtaining the weight to the nearest mg., put it in an envelope, transport it to the sampling place, and place it in the holder of the high volume sampler. Replace the filter housing, with the filter paper facing up, and turn on the motor. Note the initial sampling rate, the time, and the weather conditions. Return to the sampling place as close to 24 hours later. Again note the rotameter reading, the time, and the weather conditions. Stop the motor, take out the filter, fold it once along the long axis, press it flat, and return to the laboratory.

**Determination.**—Dry the filter in an oven overnight at 100°C to cool, and reweigh to the nearest mg. The increase in weight is the total suspended particulate matter.

**Calculation.**—The high volume sampler and its rotameter are calibrated against a total gas volume instrument. Assuming that the increase in weight is a straight line function of the clogging of the pores of the filter, the volume of air sampled by adding the initial and final rotameter readings, and dividing by two. Multiply by the initial sampling rate to get the total volume of air sampled. Multiply by the calibration factor to press the results in milligrams per cubic meter:

$$\text{mg./cu. meter} = \frac{\text{mg.}}{V \times 0.02832}$$

where mg. = weight of the deposit in milligrams,  
and  $V$  = corrected volume of air sampled in cubic feet.

The suspended particulate matter can then be analyzed by the National Air Sampling Network of the National Institute for Environmental Health Service, Department of Health, Education, and Welfare.<sup>8</sup>

<sup>6</sup> Catalog No. CT-25310, also MSA No. 1106B, Mines Safety Appliances Co., Pittsburgh, Pa.

<sup>7</sup> Silverman, L., and Viles, F. J., *J. Ind. Hyg. Toxicol.*, 30, 124, 1947.

<sup>8</sup> Air Pollution Measurements of the National Air Sampling Network, Particulate Matter, 1953-1957, Public Health Serv., Publication 637

For ordinary work, the temperature and pressure correction may be neglected and the sulfur dioxide concentration can be computed by:

$$\text{SO}_2 \text{ (p. p. m.)} = \text{ml. NaOH} \times 0.002 \times 0.027.$$

### SULFURIC ACID AND SULFUR TRIOXIDE

The conversion of sulfur dioxide to sulfur trioxide in the general atmosphere is slow. Consequently, except in certain industrial atmospheres, and under special conditions, the concentration of sulfur trioxide and sulfuric acid in the air is very low.

#### FILTER PAPER METHOD

Specially prepared filter papers are employed in the method devised by Mader, Hamming, and Bellin,<sup>11</sup> for trapping the sulfuric acid aerosol from the air being sampled. Sulfur dioxide does not interfere.

*Apparatus.*—Two pieces of Pyrex tubing, 15 mm. I.D. with ground flared ends 30 mm. in diameter, are coupled together by means of two perforated metal collars that can be clamped together and pressed tight with the aid of machine bolts and knurled nuts.

*Filter Paper Discs.*—Wash large, 18.5-cm. Whatman No. 4 filter papers by leaching with successively large quantities of distilled water over a long period of time. Five 12-hour leachings with 500 ml. of water are generally adequate. Use a 19-cm. Pyrex crystallizing dish for the washing. Dry the filter papers in an oven at 100°C.; cut each washed and dried filter with the aid of a cutting tool into 1-inch discs; and store these in a dry, clean container. Obtain the pH of each batch of filter paper discs by placing 2 discs, chosen at random, into 20 ml. of carbon dioxide-free water of known pH. Macerate the discs thoroughly with the aid of two glass rods, in order to make a slurry of paper pulp. Allow the mixture to stand for three minutes and determine the pH with a meter. Determine the uniformity of pH in the filter paper discs by repeating the test with two more samples of discs. If the three pH tests indicate a consistency of 0.03 pH unit and a deviation of not more than 0.1 pH unit from that of the water used in the measurement, the filter paper batch is considered satisfactory for the estimation of sulfuric acid aerosol.

*Procedure.*—Put two filter paper discs into the paper holder. Pull air through the filters at a rate of 50 to 60 c.f.h., recording the pressure drop through the filter and the air temperature. Remove the filter discs after sampling for one hour and place them in a dry, clean container. Bring the discs back to the laboratory. Macerate them in 20 ml. of distilled water. Measure the pH and titrate with 0.002 *N* sodium hydroxide solution. Use a pH meter for the determination of the end point, which is considered to be that of carbon dioxide-free water, corrected for filter paper batch acidity or alkalinity.

*Calculation.*—The acidity, as sulfuric acid in parts per million, can be computed by the following expression:

$$\text{H}_2\text{SO}_4 \text{ (p. p. m.)} = \frac{\text{ml. base} \times N \times 0.049 \times 22.41 \times 10^6}{98 \times 28.32 \times \text{cubic feet air at STP}}.$$

<sup>11</sup> Mader, P. P., Hamming, W. J., and Bellin, A., *Anal. Chem.*, **22**, 1181, 1950.



**Procedure.**—Draw 38.2 l. (1.35 cu. ft.) of the air to be sampled through 10.0 ml. of sodium tetrachloromercurate(II) solution, keeping the sampling rate under 0.2 c.f.m. to avoid loss of sulfur dioxide. Add 1.0 ml. of the acidified pararosaniline solution and 1.0 ml. of the formaldehyde solution to the 10.0 ml. of the sample solution. Treat a blank of 10.0 ml. of sodium tetrachloromercurate(II) solution in the same manner. Allow the mixtures to stand for 20 to 30 minutes, for full color development, and read the absorbency of the test solution compared to the blank at 560 m $\mu$ .

Prepare a standard curve using known solutions of sodium bisulfite or metabisulfite in sodium tetrachloromercurate(II), and read the concentration of sulfur dioxide from the standard curve. Each microgram of sulfur dioxide is equivalent to 0.01 p. p. m. in the air for a 38.2-l. sample. A precipitate is formed if sulfides are present, and must be removed by centrifugation or filtration. Nitrites may interfere. Samples may be collected in the field with sequence samplers and may be analyzed within a working day with no loss of sulfur dioxide attributable to either volatilization or oxidation.

### HYDROGEN PEROXIDE METHOD

The sulfur dioxide from the air is trapped in an impinger, or bubbler, containing a dilute solution of hydrogen peroxide. The sulfuric acid formed is titrated with standard sodium hydroxide solution to determine the amount of sulfur dioxide trapped.<sup>10</sup> This method estimates total acid in the air and is not specifically for sulfur dioxide.

**Reagents.** **Hydrogen Peroxide Absorbing Solution.**—Dilute with water 17 ml. of 3% hydrogen peroxide solution to 1 liter, and adjust the pH to 4 with dilute nitric acid, or if required, dilute sodium hydroxide solution.

**Sodium Hydroxide Solution (0.002 N).**—Dilute 1 N sodium hydroxide solution to approximately 0.002 N, and standardize against 0.002 N sulfuric acid. Standardize the sulfuric acid gravimetrically by the barium sulfate method, as detailed elsewhere in the text.

**Mixed Indicator Solution.**—Dissolve 0.6 g. of bromocresol green and 0.4 g. of methyl red in 1 liter of methyl alcohol.

**Procedure.**—Add 3 drops of mixed indicator solution to 75 ml. of absorbing solution in a large impinger and titrate with 0.002 N sodium hydroxide solution until the red color disappears and a green fluorescence appears. Attach the impinger to its train, including the rotameter and pump to measure the volume of air being drawn, and pass air through the peroxide absorbing solution for 30 minutes at a rate of 1 c.f.m. Note the temperature and barometric and vapor pressures. Titrate the absorbing solution at the end of the sampling period with the standard sodium hydroxide solution until the reappearance of the green fluorescence, and note the volume of sodium hydroxide solution used.

**Calculation.**—Calculate the concentration of sulfur dioxide with the following formulas:

$$\text{SO}_2(\text{p. p. m.}) = \frac{\text{ml. NaOH} \times 0.002 \times (273 + t^\circ\text{C.}) \times 1.45}{\text{volume air sampled in cubic feet}}$$

<sup>10</sup> Greenburg, L., and Jacobs, Morris B., Ind. Eng. Chem., 48, 1517, 1956.

For ordinary work, the temperature and pressure correction may be neglected and the sulfur dioxide concentration can be computed by:

$$\text{SO}_2 \text{ (p. p. m.)} = \text{ml. NaOH} \times 0.002 \times 0.027.$$

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<sup>11</sup> Mader, P. P., Hamming, W. J., and Bellin, A., *Anal. Chem.*, **22**, 1181, 1950.

## HYDROGEN SULFIDE

The method of choice for the determination of hydrogen sulfide in air pollution control work is the methylene blue method, in particular, the Jacobs, Braverman, and Hochheiser variation.<sup>12</sup> The atmosphere to be tested is bubbled through an alkaline suspension of cadmium hydroxide in a macro impinger at rates as high as 1 c.f.m. The sulfides trapped in this manner are converted to methylene blue.

**Reagents.** *Amine-sulfuric Acid Stock Solution.*—Add 12 g. of *N,N*-dimethyl-*p*-phenylenediamine to a cooled mixture of 30 ml. of water and 50 ml. of concentrated sulfuric acid. Stir until solution is complete.

*Amine-sulfuric Acid Test Solution.*—Dilute 25 ml. of stock solution to 1 liter with 1:1 sulfuric acid.

*Ferric Chloride Solution.*—Dissolve 100 g. of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in sufficient water to make 100 ml. of solution.

*Absorption Mixture.*—Dissolve 4.3 g. of cadmium sulfate,  $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ , in water. Dissolve 0.3 g. of sodium hydroxide in water. Add the sodium hydroxide solution to the cadmium sulfate solution and dilute to 1 liter. Stir well before using.

**Standard Curve.** (a) *Colorimetrically by Klett-Summerson Colorimeter.*—Add separately 0, 1, 3, 5, 7, and 9  $\mu\text{g.}$  of hydrogen sulfide equivalent, to 50-ml. volumetric flasks containing 45 ml. of alkaline cadmium absorption mixture. Add 0.6 ml. of amine test solution and 1 drop of ferric chloride solution, stirring after each addition. Dilute each to 50 ml., allow to stand for 30 minutes, and transfer the first mixture, containing no hydrogen sulfide, to the colorimeter cell. Insert the red filter, place the cell in position, and adjust the reading to zero. Read the transmission of the five remaining mixtures. Plot the optical density versus concentration in micrograms.

(b) *Spectrophotometrically by Coleman Spectrophotometer.*—Add separately 0, 1, 2, 3, and 4  $\mu\text{g.}$  of hydrogen sulfide equivalent to 20 ml. of absorption mixtures, contained in 25-ml. volumetric flasks. Add 0.6 ml. of amine test solution and 1 drop of ferric chloride solution. Stir after each addition. Then dilute to volume and allow to stand 30 minutes. Set the spectrophotometer at 670  $m\mu$ ; place the first mixture, containing no hydrogen sulfide, in a cuvet; set the instrument galvanometer to read 100; and read the remaining standards in the sample cuvet, in increasing order of concentration. Note the optical density, and plot the optical density against hydrogen sulfide concentration in micrograms.

**Procedure.** (a) *Colorimetric Variation.*—Place 50 ml. of absorption mixture in a large impinger and pass air through the apparatus for 30 minutes at a rate of 1 c.f.m. Add 0.6 ml. of amine test solution and 1 drop of ferric chloride solution to the impinger, stirring after each addition. Transfer to a 50-ml. volumetric flask, make up to volume, and allow to stand for 30 minutes. To 45 ml. of absorption mixture in a 50-ml. volumetric flask, add 0.6 ml. of amine test reagent and 1 drop of ferric chloride solution; stir after each addition; make up to volume, allow to stand for 30 minutes; and use as a reference in setting the instrument to zero. Read the optical density of the sample, and obtain the concentration of hydrogen sulfide from the standard curve.

(b) *Spectrophotometric Variation.*—Take 25 ml. of the final mixture of the sample and the reference solution, and read in a spectrophotometer at 670  $m\mu$ .

<sup>12</sup> Jacobs, Morris B., Braverman, M. M., and Hochheiser, S., *Anal. Chem.*, 29, 1349, 1957.

**Calculation.**—Compute the results from the following equation:

$$\text{H}_2\text{S (p. p. b.)} = \frac{\mu\text{g. H}_2\text{S} \times 719}{\text{volume of air sampled in liters}}.$$

This calculation is set empirically at 25°C. and 760 mm. To correct for conditions of temperature and pressure, the customary gas laws can be employed. As only half the total amount of sulfide trapped is read in the spectrophotometric variation, it is necessary to double the result of the above expression.

The method detailed is suitable for concentrations of 20 p. p. b. or less. For higher concentrations, a variation using a midjet impinger has been detailed by Jacobs, Braverman, and Hochheiser. The methods for the determination of sulfur-bearing air contaminants have been discussed in considerable detail by Jacobs.<sup>13</sup>

## NITROGEN OXIDES

The chemistry of the nitrogen oxides is discussed elsewhere. The nitrogen oxides in the air are commonly determined by variations of the Griess-Ilosvay diazotization reaction that depends on four components; these are the substance that can be diazotized, nitrite ion, a proper acidity, and a coupling agent. It should be noted that unless the nitrate present in the test sample is reduced to nitrite and the nitric oxide is oxidized to nitrogen dioxide, these substances are not determined by the diazotization method.

### JACOBS AND HOCHHEISER METHOD

Nitrogen dioxide can be estimated in the presence of much higher concentrations of sulfur dioxide by the Jacobs and Hochheiser method,<sup>14</sup> a variation of the Greiss-Ilosvay reaction. Air is aspirated through a fritted-glass bubbler containing 0.1 *N* alkali solution. Any sulfur dioxide that is present and absorbed is oxidized to sulfate with hydrogen peroxide, so that it does not interfere. The absorbed nitrogen dioxide-nitrogen tetroxide is determined colorimetrically as the azo dye by using it to diazotize sulfanilamide in phosphoric acid and then coupling with *N*-(1-naphthyl)-ethylenediamine dihydrochloride. The method is suitable for concentrations of nitrogen dioxide of the order of parts per hundred million.

Sampling can be performed with individual bubblers or with a sequence sampler so that 24 one-hour samples can be obtained.

**Reagents.** **Sodium Hydroxide Absorbing Solution.**—Add 2 ml. of butyl alcohol per liter of 0.1 *N* sodium hydroxide solution, to increase the foaming action, and to assist in trapping the nitrogen dioxide.

***N*-(1-naphthyl)-ethylenediamine Dihydrochloride Solution.**—Dissolve 0.1 g. of the coupling agent in distilled water and make up to 100 ml. with water.

**Sulfanilamide Solution.**—Dissolve 20 g. of sulfanilamide in 1 liter of water containing 50 ml. of phosphoric acid.

**Standard Sodium Nitrite Solution.**—Dissolve 150 mg. of sodium nitrite,  $\text{NaNO}_2$ , in 1 liter of water. Dilute 10 ml. of this solution to 100 ml.; each milliliter of this solution contains 10  $\mu\text{g.}$  of  $\text{NO}_2$ .

**Standard Curve.**—Add 0.2, 0.6, 0.8, and 1.0 ml. of standard sodium nitrite solution to 35 ml. of absorbing reagent contained in 50-ml. Nessler tubes. Add 1 drop

<sup>13</sup> Jacobs, Morris B., in McCabe, L. C. (ed.), *Air Pollution*, McGraw-Hill, New York, 1952; in Lodge, J. P., Jr., (ed.), *Atmospheric Chemistry of Chlorine and Sulfur Compounds*, Am. Geophys. Union, Washington, D. C., 1959, 24.

<sup>14</sup> Jacobs, Morris B., and Hochheiser, S., *Anal. Chem.*, 30, 426, 1958.

of 1% hydrogen peroxide solution, 10 ml. of sulfanilamide solution, 1 ml. of coupling reagent; mix after each addition; and dilute to 50 ml. Read in a spectrophotometer at 550  $m\mu$ , using the reagent blank to set 100% transmission. Plot the readings against the nitrite concentration in micrograms, to obtain the curve.

**Procedure.**—Aspirate air at 1.3 l. per minute through 30 to 35 ml. of absorbing reagent in a fritted bubbler. Transfer the sample to a 50-ml. Nessler tube. Add 1 drop of hydrogen peroxide solution (1%) and mix. Add 10 ml. of sulfanilamide reagent and then 1 ml. of *N*-(1-naphthyl)-ethylenediamine reagent. Dilute to 50 ml. and mix. Allow to stand for 30 minutes and determine the optical density in a Coleman spectrophotometer at 550  $m\mu$ , using a reagent blank as the reference, and 20 x 40 mm. matched cuvetts.

**Calculation.**—The concentration of nitrogen oxides in air as nitrogen dioxide is generally expressed in parts per hundred million. For a 52-l. air sample at 25°C. and 760 mm., 1  $\mu$ g. of  $\text{NO}_2$  is equivalent to 1 p.p.h.m.

### NITROGEN OXIDES AS NITRATE

The nitrogen oxides can be absorbed as detailed, and oxidized to nitrate, which can be determined by the phenoldisulfonic acid method as detailed elsewhere in this text, or by the xylenol method.<sup>15</sup>

### OTHER METHODS

Other methods for the determination of nitrogen oxides as nitrite include: the official British method for industrial hygiene purposes,<sup>16</sup> in which the nitrogen oxides are absorbed in a reagent consisting of sulfanilic acid, alpha-naphthylamine, and acetic acid, Saltzman,<sup>17</sup> who, following Jacobs,<sup>18,19</sup> substituted *N*-(1-naphthyl)-ethylenediamine dihydrochloride for the alpha-naphthylamine; and an ASTM method,<sup>20</sup> which also uses this variation. These methods are discussed in detail by Jacobs.<sup>19</sup>

### AMMONIA

A variation of the Nessler method is used for the determination of ammonia and ammonium compounds in the atmosphere.

**Reagents.** **Nessler Reagent.**—This is commercially available or can be prepared in a number of ways. The method of Folin<sup>21</sup> is preferable. Nessler's solution is an alkaline solution of the double iodide of mercury and potassium ( $\text{HgI}_2 \cdot 2\text{KI}$ ). Transfer to a 200-ml. flask 30 g. of potassium iodide and 22.5 g. of iodine; add 20 ml. of water and, after solution is complete, an excess of metallic mercury, i.e., approximately 30 g. Shake the flask continuously and vigorously until the dissolved iodine has nearly all disappeared; this takes about 7 to 15 minutes. The solution becomes hot. When the red iodine solution has begun to become visibly pale, although still red, cool it in running water and continue shaking until the

<sup>15</sup> Yagoda, H., and Goldman, F. H., *J. Ind. Hyg. Toxicol.*, 25, 440, 1913.

<sup>16</sup> Dept. Sci. Ind. Research Brit., Leaflet 5, 1939.

<sup>17</sup> Saltzman, B. E., *Anal. Chem.*, 26, 1949, 1951.

<sup>18</sup> Jacobs, Morris B., *War Gases—Their Identification and Decontamination*, Interscience Publishers, Inc., New York, 1942.

<sup>19</sup> Jacobs, Morris B., *The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents*, 2nd Ed., Interscience Publishers, Inc., New York, 1949.

<sup>20</sup> ASTM Standard, Designation D1607-58T.

<sup>21</sup> Jacobs, Morris B., *The Chemical Analysis of Foods and Food Products*, D. Van Nostrand and Co., Inc., Princeton, 1958.

reddish color of the iodine has been replaced by the greenish color of the double iodide. The whole operation generally takes 15 minutes. Test a portion of the solution with starch solution. Unless the starch test is positive, the solution may contain mercurous compounds. Decant the solution, washing the mercury and flask with water. Dilute the solution and washings to 200 ml. and mix well. If the cooling was begun in time, the resulting reagent is clear enough for immediate dilution with 10% alkali and water, and the finished solution can be used at once for Nesslerization. From this stock solution of potassium mercuric iodide, prepare the final Nessler's solution by adding the 200 ml. of the double iodide solution to 975 ml. of an accurately prepared 10% sodium hydroxide solution. Mix thoroughly and allow to clear by permitting to stand.

**Absorbing Solution.**—Add 1 ml. of concentrated sulfuric acid to 10 l. of distilled water.

**Alkaline Rochelle Salts.** Dissolve 10 g. of Rochelle salts, potassium sodium tartrate  $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ , in 200 ml. of 0.01 *N* sodium hydroxide solution.

**Standard Curve.**—Prepare a standard solution from ammonium chloride to contain 1  $\mu\text{g}$ . of ammonia,  $\text{NH}_3$ , per milliliter. Transfer, to a series of large impingers, 0, 5, 10, 15, 20, 25, and 30 ml. of the standard solution, and make up to a volume of 50 ml. Continue with the method as detailed in the procedure.

**Procedure.**—Transfer 50 ml. of absorbing solution to a large impinger. Connect the impinger to its sampling train and draw air through the absorbing solution at a rate of 1 c.f.m. for 30 minutes. Transfer the contents of the impinger to a 50-ml. volumetric flask, or to a 50-ml., glass-stoppered Nessler tube. The volume of the sample will be about 46 ml. as a result of the loss of water due to evaporation during the sampling. Add 46 ml. of absorbing solution to another Nessler tube and use as the blank. Add 4 ml. of Nessler reagent to each tube or flask, mix thoroughly, and read exactly 10 minutes later in a Klett-Summerson photoelectric colorimeter using the No. 54 (green) filter. Use the 50-ml. glass cells for the reading, and employ the reagent blank to set the zero.

If a cloudy solution forms after the addition of the Nessler reagent, add alkaline Rochelle salts reagent, drop by drop with constant shaking, until the cloudiness disappears.

Refer to the standard curve to obtain the micrograms of ammonia in the sample, and compute to the volume of 30 cu. ft. sampled.

## OZONE AND OXIDANTS

No really satisfactory method for the determination of ozone, *per se*, in air is available. One of the difficulties stems from the fact that there is no satisfactory method of preparing standard curves from ozone. The method most often used is a variation of the Smith and Diamond<sup>22</sup> alkaline iodide method.

### ALKALINE IODIDE METHOD

Ozone and oxidants are absorbed from the atmosphere by an alkaline iodide solution. This solution is oxidized with hydrogen peroxide to avoid interference of sulfur dioxide, and the pH is adjusted to eliminate the interference of nitrogen dioxide. When acidified, iodine is liberated from the hypoiodite formed on absorption of the oxidant, and the amount of triiodide produced is determined spectrophotometrically by measuring the absorption of light at 352  $\text{m}\mu$ .

**Reagents.** **Alkaline Iodide Absorption Solution.**—Dissolve 10 g. of potassium

<sup>22</sup> Smith, R. G., and Diamond, P., *Am. Ind. Hyg. Assoc. Quart.*, 13, 235, 1952.

iodide and 4 g. of sodium hydroxide in water, and make up to 1 liter with water. This solution is approximately 1% with respect to potassium iodide, and 0.1 N with respect to sodium hydroxide.

**Hydrogen Peroxide Solution (1%).**—Prepare a 1% hydrogen peroxide solution from 30% hydrogen peroxide.

**Standard Curve.**—Prepare a potassium iodate solution in which 1 ml. is equivalent to 1.5  $\mu$ g. of potassium iodate; this is equivalent to 1  $\mu$ g. of ozone. Add aliquots of iodate solution equivalent to 1 to 15  $\mu$ g. of ozone, in a series, to 50-ml., glass-stoppered Nessler tubes containing 30 ml. each of absorbing solution. Do not add peroxide, boil, or pass air through these solutions. Add sufficient water to bring each volume up to 40 ml. Then add successively for each standard, just before reading 3 N acetic acid (1:5), to volume, stopper, mix, and read in the spectrophotometer at 352  $m\mu$ , using water as the zero reference. Prepare a curve plotting absorbance against micrograms.

**Procedure.**—Place 30 ml. of absorbing solution into each of two large impingers in series, and dilute to 75 ml. Draw air through the impingers at a rate of 1 c.f.m. for 30 minutes. The second impinger serves as a blank of the air washed free of oxidant. Transfer the contents of each impinger to 100-ml. beakers, and add 1 drop of 1% hydrogen peroxide solution to oxidize the sulfite formed from the sulfur dioxide absorbed to sulfate. Boil the solution in each beaker down to 40 ml. to decompose the excess hydrogen peroxide; cool, and transfer to 50-ml., glass-stoppered Nessler tubes. Add 3 N acetic acid (1:5) to reduce the pH to 3.8 (about 10 ml. is required), mix, and transfer some of the test solution to a test-tube cuvet of a Coleman or equivalent spectrophotometer, set at 352  $m\mu$ , using water as the zero reference. The optical density of the test sample is considered to be the optical density of the sample solution minus the optical density of the blank.

One-cm. Corex cells are suitable with a Beckman model DU spectrophotometer. The blue-sensitive phototube should be used with an ultraviolet filter and a tungsten light source. Greater sensitivity can be obtained by using the absorption peak at 289  $m\mu$ , but if this wavelength is used, quartz cells and an ultraviolet light source are required. A standard curve must be made at this wavelength also.

**Calculations.**—One  $\mu$ g. of ozone  $O_3$  yields 5.29  $\mu$ g. of iodine  $I_2$ ; consequently, 1  $\mu$ g. of iodine is equivalent to 0.189  $\mu$ g. of ozone. The concentration of oxidants in parts per billion may be computed from the expression

$$\text{oxidants as } O_3 \text{ (p.p.b.)} = \frac{\text{mg. } O_3 \times 509 \times 1000}{\text{volume of air in cubic feet} \times 28.32}$$

### OTHER METHODS

Other methods for ozone and oxidants are: the sulfamic acid variation of the alkaline iodide method detailed by Jacobs;<sup>23</sup> the sulfamic acid, neutral buffered iodide method of McQuain and co-workers;<sup>24</sup> the modified Smith and Diamond method of the ASTM,<sup>25</sup> the titrimetric method of Ehmer<sup>26</sup> and of Wadelin;<sup>27</sup>

<sup>23</sup> Jacobs, Morris B., *The Chemical Analysis of Air Pollutants*, Interscience Publishers, Inc., New York, 1960.

<sup>24</sup> McQuain, R. H., Leavitt, J. M., Wanta, R. C., and Frisbie, W. W., *Air Pollution Control Assoc. Meeting*, Philadelphia, May, 1958.

<sup>25</sup> ASTM Standard Designation: 1609-58T.

<sup>26</sup> Ehmer, A., *J. Atmospheric Terrest. Phys.*, **2**, 189, 1952.

<sup>27</sup> Wadelin, C. W., *Anal. Chem.*, **29**, 441, 1957.

the Haagen-Smit and Fox phenolphthalein method;<sup>28</sup> the Bradley and Haagen-Smit rubber cracking method;<sup>29</sup> and the ferrous thiocyanate method of Todd.<sup>30</sup>

## CARBON MONOXIDE

The methods of choice for the determination of carbon monoxide in air and in exhaust gases, namely, pressurized, nondispersive, and infrared spectrophotometers,<sup>31</sup> are instrumental and, for the most part, expensive. The indicator tube method, described below, is relatively inexpensive, and can be employed for this purpose.

### NBS INDICATOR TUBE METHOD

The National Bureau of Standards' carbon monoxide indicator tube<sup>32</sup> contains highly purified silica gel that is impregnated with ammonium molybdate and a solution of palladium or palladium oxide, digested in sulfuric acid, forming a palladium silicomolybdate. When this gel is exposed to carbon monoxide, a molybdenum blue is formed, the depth of color varying from faint green to blue, in proportion to the amount of carbon monoxide present in the air drawn through the tube. Such tubes are available commercially.

The tubes were originally designed for relatively higher concentrations of carbon monoxide than are normally present in the outside atmosphere, except in areas of heavy motor vehicle traffic. They can, however, be adapted for analyses in which the concentration of carbon monoxide is considerably lessened, of the order of 1 to 2 p. p. m., by substituting a small vacuum pump for the aspirator bulb used with the tube.<sup>33</sup>

**Procedure.**—Break the tips of an NBS carbon monoxide indicator tube and insert the tube with the unfilled end in the sampling line directed toward the pump, that is, place the tube so that the incoming air stream has to pass through the longer section of silica gel. Draw air through the detector tube at a rate of 100 ml. per minute, with the aid of a small vacuum pump. Note the time that the pump is started, and observe the indicator gel carefully to determine the time the first green of the comparison color chart provided with the tube is obtained. Record the total elapsed time.

**Calculation.**—Compute the concentration of carbon monoxide in the air sample from the time of sampling, the volume of air drawn through the tube, and the color change. It is known that five squeezes of the aspirator bulb yield a color change that matches the first green when the carbon monoxide concentration is 0.001%. From this relationship, the following expression can be derived:<sup>33</sup>

$$\text{CO (p. p. m.)} = \frac{24}{\text{time in minutes}}.$$

<sup>28</sup> McCabe, L. C., *Ind. Eng. Chem.*, 45, No. 9, 111A, 1953.

<sup>29</sup> Bradley, C. E., and Haagen-Smit, A. J., *Rubber Chem. Technol.*, 24, No. 4, 750, 1951.

<sup>30</sup> Todd, G. W., *Anal. Chem.*, 27, 1490, 1955.

<sup>31</sup> Waters, J. L., and Hartz, N. W., *An Improved Luft-type Infrared Gas and Liquid Analyzer*, Instrument Soc. Amer., Meeting, Houston, 1951; Jacobs, Morris B., Hochheiser, S., and Braverman, M. M., *J. Air Pollution Assoc.*, 9, No. 2, 110, 1959.

<sup>32</sup> Jacobs, Morris B., *The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents*, 2nd Ed., Interscience Publishers, Inc., New York, 1949; Shepherd, M., *Anal. Chem.*, 19, 77, 1947.

<sup>33</sup> Jacobs, Morris B., *The Chemical Analysis of Air Pollutants*, Interscience Publishers, Inc., New York, 1960.



The concentration of carbon monoxide in flue gases can be determined with the American Gas Association variation of the iodine pentoxide method.<sup>33, 34</sup>

## ORGANIC POLLUTANTS

The principal organic air contaminants may be grouped as: (1) saturated and unsaturated aliphatic hydrocarbons such as methane, hexane, ethylene, and acetylene; (2) aromatic hydrocarbons such as benzene and toluene; (3) polynuclear hydrocarbons like benzo[a]pyrene; (4) aldehydes such as formaldehyde and acrolein; (5) phenols; and (6) amines. Adequate chemical methods are available for aldehydes, benzene, phenols, and acetylene. These methods will be described.

### ALDEHYDES

#### SULFOXYLATE METHOD

The method most commonly used for the determination of aldehydes as air contaminants is the sulfoxylate method of Goldman and Yagoda.<sup>35</sup> The aldehydes are absorbed from the air by bisulfite. The complex formed is stable in slightly acid and neutral solutions, but is decomposed when the solution is made distinctly alkaline. All aldehydes are trapped in this method but the estimation is usually calculated to formaldehyde.

**Reagents. Bisulfite Solution.**—Dissolve 9 g. of sodium metabisulfite in almost 1 liter of water, containing 1 ml. of concentrated sulfuric acid, and dilute to 1 liter.

**Iodine Solution (8%).**—Dissolve 160 g. of potassium iodide in a small amount of water, and dissolve 80 g. of iodine in this concentrated solution. Dilute to 1 liter with water. This strong iodine solution need not be standardized.

**Standard Iodine Solution (0.001 N).**—Make a solution containing exactly 126.9 mg. of iodine per liter.

**Sodium Thiosulfate Solution.**—Dissolve 1.5 g. of sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , and 5 g. of sodium bicarbonate in water, and dilute to 100 ml. This solution need not be standardized.

**Buffer Solution.**—Make a solution containing 80 g. of sodium carbonate and 20 ml. of glacial acetic acid per liter with water. Store in a refrigerator.

**Procedure.**—Transfer 75 ml. of the bisulfite-absorbing solution to a large impinger, and attach it to a train consisting of a trap, flowmeter, temperature and pressure measuring devices, and a vacuum pump. Pull air through the absorbing solution at 1 c.f.m. for 30 minutes. Place the impinger in an ice bath and keep it immersed for 30 minutes. Add 1 ml. of 1% starch indicator solution, and titrate with the 8% iodine solution to a blue color. Record the volume of 8% iodine solution consumed, for it is necessary to know if a 5-ml. excess of sodium bisulfite-absorbing solution was present at the end of the sampling period. Discharge the blue color by adding the sodium thiosulfate solution drop by drop, and then readjust to a faint blue color with the 0.001 N iodine solution. Put the impinger back into the ice until it is thoroughly chilled. Add 50 ml. of cold buffer solution, and keep the reaction mixture in the ice bath for an additional 10 minutes to avoid the fading of the end point in final titration. Titrate again with 0.001 N iodine solution to determine the amount of bisulfite liberated.

<sup>34</sup> Am. Gas Assoc. Laboratories, Cleveland, Ohio.

<sup>35</sup> Goldman, F. H., and Yagoda, H., Ind. Eng. Chem., Anal. Ed., 15, 377, 1943.

**Calculation.**—For routine work, without correcting for temperature and pressure variations, the aldehyde concentration can be computed as follows:

$$\text{Aldehydes, as HCHO (p. p. m.)} = \text{ml. } 0.001 \text{ N I}_2 \times 0.013.$$

### OTHER METHODS

A number of other methods have been employed for the determination of aldehydes in air and in exhaust gases. Among these are the Schiff-Elvove rosaniline-sulfite method,<sup>36</sup> the Schryver phenylhydrazine method, which can be used to distinguish between formaldehyde and total aldehydes,<sup>37</sup> the Jacobs and Eastman variation of the phenylhydrazine method,<sup>38</sup> and the Cohen and Altshuller method for acrolein.<sup>39</sup>

### BENZENE

Ketones such as acetone, ethyl methyl ketone (butanone), and other ketones react with *m*-dinitrobenzene to yield violet colors. This method for the determination of benzene was developed by the U. S. Bureau of Mines.<sup>40</sup> In the Dolin<sup>41</sup> modification, the color obtained with benzene is stable in acetic acid, whereas the colors formed with other aromatic compounds disappear rapidly.

### BUTANONE METHOD

**Absorbing Reagent.**—Mix equal volumes of concentrated sulfuric acid and fuming nitric acid.

**Procedure.**—Pass a known volume of the air being sampled through two midjet impingers in series containing 2 to 3 ml. of absorbing solution. After sampling is completed, allow to stand for 10 minutes and cautiously dilute with 25 ml. of water. Cool the mixture and extract the nitrated material with 25 ml. of ethyl ether. Draw off the aqueous layer and discard. Wash the ether layer with 25 ml. of water. Discard the water layer and transfer the ether layer to a 100-ml. volumetric flask. Make to volume with 95% alcohol. Transfer a 10-ml. aliquot to a test tube, add 1 ml. of butanone and 2 drops of 40% sodium hydroxide solution, shake the mixture, and allow to stand for 10 minutes. In the presence of benzene a crimson color is formed.

Add 5 drops of glacial acetic acid, stir the test tube contents, and allow to stand for an additional 10 minutes. At the end of this period compare with known concentrations of benzene treated in an analogous manner, or read the

<sup>36</sup> Elvove, E., *Ind. Eng. Chem.*, **9**, 295, 1917.

<sup>37</sup> Rounds, F. G., and Pearsall, H. W., *Diesel Exhaust Odor*, S.A.E. Natl. Diesel Engine Meeting, Chicago, 1956.

<sup>38</sup> Jacobs, Morris B., Eastman, E. L., and Shepard, D. L., *J. Am. Pharm. Assoc., Sci. Ed.*, **40**, 365, 1951; Jacobs, Morris B., *The Chemical Analysis of Air Pollutants*, Interscience Publishers, Inc., New York, 1960.

<sup>39</sup> Cohen, I. R., and Altshuller, A. P., *Anal. Chem.*, **33**, 726, 1961.

<sup>40</sup> Schrenk, H. H., Pearce, S. J., and Yant, W. P., *U. S. Bur. Mines, Rept. Invest.*, **3287**, 1935; **3302**, 1936; Jacobs, Morris B., *The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents*, 2nd Ed., Interscience Publishers, Inc., New York, 1949.

<sup>41</sup> Dolin, B. H., *Ind. Eng. Chem., Anal. Ed.*, **15**, 242, 1943; *N. Y. State Ind. Bull.*, **25**, No. 7, 1946.

transmission and calculate the amount of benzene from a standard curve. Other methods for the determination of benzene have been discussed by Jacobs.<sup>42</sup>

### ACETYLENE

Hughes and Gorden<sup>43</sup> modified the cuprous acetylide reaction so that it could be used for the determination of acetylene in air in the range of parts per billion.

**Reagents.** Ammoniacal Cupric Chloride Solution.—Dissolve 1.5 g. of cupric chloride and 3 g. of ammonium chloride in 20 ml. of concentrated ammonium hydroxide solution, and dilute to 50 ml. with water.

**Hydroxylamine Solution.**—Dissolve 5 g. of hydroxylamine hydrochloride in 50 ml. of water.

**Ammoniacal Cuprous Chloride Solution.**—Mix 1 volume of the ammoniacal cupric chloride solution with 4 to 5 volumes of the hydroxylamine solution.

**Sampling.**—Use a train consisting of a probe, a U-tube containing glass wool to serve as a trap, a detector tube containing adsorbent silica gel, and a vacuum pump with glass to glass or Tygon tube connections.

**Procedure.**—Immerse the U-tube and detector tube in a freezing bath containing acetone and dry ice. Draw air at 0.2 l. per minute for 10 to 50 minutes, depending on whether the concentration is below 1 p.p.m. Remove the tube from the bath and allow to warm up to ambient temperature; add the ammoniacal cuprous chloride reagent. Note the development of a pink, red to brown color, which is stable for 48 hours. Compare with standards made by passing known concentrations of acetylene in pure air through similar detector tubes.

### PHENOLS

A number of methods for the determination of phenol are detailed throughout the text. These can be used, with but slight modification, for the determination of phenols in air. A method devised by Braverman, Hochheiser, and Jacobs,<sup>44</sup> in which *p*-aminodimethylaniline sulfate is used as a reagent, can be employed to detect phenols in air in the order of parts per ten billion of air.

**Reagents.** *p*-Aminodimethylaniline Sulfate Stock Solution.—Mix 50 ml. of concentrated sulfuric acid with 30 ml. of water and cool. Add 20 g. of the amine, stirring until solution is complete. Make up to 100 ml. with additional water.

*p*-Aminodimethylaniline Sulfate Test Solution.—Dilute 5 ml. of the stock amine solution to 100 ml. with water.

**Standard Phenol Solution.**—Make a solution containing 100  $\mu$ g. of phenol per milliliter and standardize it by the bromide-bromate method. Prepare a solution containing 1  $\mu$ g. per milliliter from the stock solution by dilution.

**Standard Curve.**—Add 1, 3, 5, and 7  $\mu$ g. of phenol to 45 ml. of 0.5% sodium bicarbonate solution in a 125-ml. separatory funnel. Follow the method as detailed in the procedure. Determine the optical densities at 600  $m\mu$ , using a final volume of 10 ml. and a blank as the reference.

**Procedure.**—Aspirate air at a rate of 1 c.f.m. through 45 ml. of 0.5% sodium bicarbonate solution in a fritted bubbler. Transfer the sample solution to a 125-ml.

<sup>42</sup> Jacobs, Morris B., and Scheffan, L., *The Chemical Analysis of Industrial Solvents*, Interscience Publishers, Inc., New York, 1953.

<sup>43</sup> Hughes, E. E., and Gorden, R., *Anal. Chem.*, **31**, 94, 1959.

<sup>44</sup> Braverman, M. M., Hochheiser, S., and Jacobs, Morris B., *Am. Ind. Hyg. Assoc. Quart.*, **18**, No. 2, 132, 1957.

separatory funnel. Add 4 drops of the amine test reagent, and then add 0.1% calcium hypochlorite solution, dropwise until the pink color changes either to blue or to colorless. Allow to stand for 5 minutes. Extract with 10 ml. of chloroform. Filter the chloroform layer through a pledget of cotton into a small test tube. Make up to 10 ml. with chloroform. Stopper the tube and allow to stand for 30 minutes. Read the optical density at 600  $m\mu$ , and calculate the concentration of phenol from the standard curve and the volume of air sampled.

## Chapter 24

# ALLOYS: IRON AND STEEL

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**Introduction.**—This chapter comprises reference methods compiled under the jurisdiction of Committee E-3 on Chemical Analysis of Metals, American Society for Testing and Materials (ASTM), 1916 Race Street, Philadelphia 3, Pa. Standard and Tentative Methods are included.

The ASTM Standard Methods are referee methods primarily; the Tentative Methods have been approved by the sponsoring committee and accepted for use pending adoption as standard. Both Standard and Tentative Methods are issued under a fixed designation E30, followed by a number that is the year of original adoption or, in the case of revision, the year of last revision; the year is followed by a T for Tentative Methods. The designation E30-60T, for example, denotes a Tentative Method, adopted in 1960.

Incorporated into the following procedures are Standard Sampling Methods (E59-57) and selected material from Recommended Practices for Apparatus and Reagents (E50-60). In addition, the chapter includes selected methods—mainly for determinations for which ASTM Methods have not been compiled. More extensive information, such as may be necessary for unusual or research analytical problems, is available in several published works.<sup>1</sup>

<sup>1</sup> ASTM, Methods for Chemical Analysis of Metals, American Society for Testing and Materials, Philadelphia, 1960; Beeghly, H. F., Ferrous Metallurgy, Reviews, Analytical Chemistry, 21, 241-6, 1949; 22, 235-8, 1950; 23, 228-31, 1951; 24, 252-8, 1952; 25, 30-6, 1953; 27, 611-14, 1955, 29, 638-43, 1957, 31, 706-12, 1959; 33, 70R-76R, 1961; BSI, Methods for the Sampling and Analysis of Iron and Steel, British Standards Institution, London (as issued); Kolthoff, I. M., and Elving, P. J. (eds), Treatise on Analytical Chemistry, Interscience Publishers, New York, 1961; Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., Chemical Analysis of Iron and Steel, John Wiley and Sons, Inc., New York, 1931; Piggott, E. C., Ferrous Analysis—Modern Practice and Theory, John Wiley and Sons, New York, 1953, Iron and Steel Institute, Special Report #68, The Determination of Gases in Metals, The Iron and Steel Institute, London, 1960; Westwood, W., and Mayer, A., Chemical Analysis of Cast Iron, and Foundry Materials, Allen and Unwin, 1952.

# STEEL, CAST IRON, OPEN-HEARTH IRON, AND WROUGHT IRON<sup>2</sup>

*Scope.*—These methods cover procedures for the chemical analysis of steel, cast iron, open-hearth iron, and wrought iron. They have been compiled as standard procedures for use in referee analyses. The analyst should check the method and technique that is used by means of a National Bureau of Standards standard sample that has a composition comparable with that of the material under test. A list of these standard samples is given in the Bureau's Supplement to *Circular C 552*.

## SAMPLING (E59-57)

### a. ROLLED AND FORGED STEEL PRODUCTS

Different parts of a piece of steel may vary in composition. For this reason, a sample from a single piece must be carefully selected if it is to be representative of that piece. To obtain an analysis representative of a melt, a number of representative pieces should be sampled and analyzed separately. In any case, the sample shall be so selected as to be thoroughly representative, and large enough to suffice for all of the required determinations. It should be remembered that the composition of the steel is changed by certain operations and that samples should be taken from the steel in its original condition.

Samples shall consist of drillings or chips cut by some machine tool without the application of water, oil, or other lubricant, and shall be free of scale, surface metal, grease, dirt, or other foreign substances. In sampling skelp, pipe, and tubes, or flat rolled stock used in the manufacture of pipe and tubes, the diameter of the drill used shall be the largest practicable within the limits of  $\frac{1}{4}$  to 1 in. If samples from other materials are taken by drilling, the diameter of the drill used shall be not less than  $\frac{1}{2}$  in., when the area of cross-section to be sampled is 16 sq. in. and under, and shall be not less than 1 in., when the area of cross-section to be sampled is over 16 sq. in. Samples shall be uniform, thoroughly mixed, and free of dust. Chips too coarse to pass a No. 16 (1190- $\mu$ ) sieve<sup>3</sup> are not recommended, nor shall long, curly drillings that will not pack closely for the carbon determination be used. In referring samples to other analysts for check analysis, pieces of the original full-size section shall be submitted, when possible, rather than cuttings, unless the latter are specifically requested.

<sup>2</sup> ASTM Designations: E30-56, and E30-60T. Reproduced with the permission of the American Society for Testing and Materials.

<sup>3</sup> Detailed requirements for these sieves are given in the Specifications for Sieves for Testing Purposes (ASTM Designation: E11), 1960 Supplement to Book of ASTM Standard, Parts 3 to 5 and 7 to 10.

**Location of Samples. Large Sections.**—For large sections, including blooms, billets, slabs, rounds, squares, shapes, etc., samples shall be taken at any point midway between the outside and the center of the piece by drilling parallel to the axis. In cases where this is not practicable, the piece shall be drilled on the side (see Fig. 24-1 (b) and (c)) but the drillings shall not be collected until they represent the portion midway between the outside and the center. The tension test specimen may be used for sampling if it conforms to the above conditions.

**Bored Forgings and Forged, Turned, and Bored Pipe.**—For bored forgings, samples shall be taken midway between inner and outer surface of the wall. For forged, turned, and bored pipe, samples shall be taken by drilling through the pipe wall, or cuttings shall be taken across the end of the tube, or millings shall be taken from a broken tensile test specimen cut from the wall of the tube.

**Thin Material.**—For thin material or material of small cross-section, such as plates, shapes, bars, etc., if the method described for large sections is not ap-

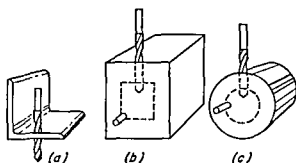


FIG. 24-1. Location of Samples for Check Analysis.

plicable, the sample shall be taken by machining off the entire cross-section, or, if this is not possible, by drilling entirely through the material at a point midway between the outside and the center (see Fig. 24-1 (a)).

**Sheets Rolled Longitudinally.**—For sheets rolled from slabs or bars longitudinally, the specimen for sampling shall be cut 2 in. in width, and across the full width of the sheet as rolled. The specimen shall be cleaned by pickling or grinding and then folded once or more by bringing the ends together and closing the bend. The sample for analysis shall be taken in the middle of this length, by milling the inside sheared edges or drilling entirely through from the flat surface. Sampling by milling is preferable. For sheets of a light gauge, more than one specimen may be taken and stacked together before folding.

**Sheets Rolled Transversely.**—For sheets rolled from slabs or bars transversely, the specimen shall be cut from the side of the sheet, halfway between the middle and end as rolled, 2 in. in width and 18 in. in length. If the sheet is No. 20 gauge (24 oz. per sq. ft. or 0.037 in. in thickness) or lighter, the specimen shall be cut from the full length of the sheet as rolled. The specimen selected shall be cleaned by pickling or grinding, and then folded once or more by bringing the ends together and closing the bend. The sample for analysis shall be taken in the middle of this length by milling the inside sheared edges or drilling entirely through from the flat surface. Sampling by milling is preferable.

**Sheets Not of the Full Size Rolled.**—Sheets cut from larger sheets, and not of the full size rolled, shall be sampled by milling or drilling the sheet in a sufficient number of places so that the sample is representative of the entire sheet. The sampling may be facilitated by folding the sheet both ways.

**Skelp and Flat Rolled Stock Used in the Production of Pipe and Tubes.**—For skelp and flat rolled stock used in the manufacture of pipe or tubes, the specimen shall be cut across the width of the material as rolled. Sampling shall be by one of the following methods (A specific method may be required by reference.): (1) chips cut by some machine tool representing the full cross-sections; (2) chips cut by some machine tool representing a half cross-section; (3) drilling through or milling across the test specimen or a 2-in. strip cut midway between edge and center; or (4) drilling through at several points across the width.

**Pipe or Tubes.**—Sampling shall be by one of the following methods: (1) chips cut by some machine tool, representing the cross-section; (2) chips cut by some machine tool, representing a half cross-section from a point adjacent to the longitudinal weld to a point 180° from the weld. Weld metal shall not be included; (3) drilling through or cutting by some machine tool across the test specimen or 2-in. coupon located 90° from weld in welded products; or (4) drilling through the pipe wall at several locations around the circumference of the pipe or tube. In sampling wrought iron pipe it is desirable that the sample represent the entire cross-section of the specimen. Sampling by milling is preferable. Complete details are included in the section on sampling wrought iron.

## b. PIG IRON

In the absence of a special agreement between the manufacturer and the purchaser, or whenever it is necessary to sample pig iron in the solid state, the sampling shall be carried out in the following manner: not less than three pigs shall be taken to represent any lot or shipment, and for lots of more than 30 tons one pig shall be taken for each 10 tons of iron; the pigs shall be selected by some means, such as the knotted rope system, that eliminates the element of personal choice; three to seven pigs, taken in the order selected, shall constitute a unit sample; for boat or barge shipments, arrangements between the seller and the purchaser may be made, if desired, in regard to taking fewer pigs per ton; if for any reason it is desirable to fracture the pigs, they may be broken in two, and one portion of each of the original pigs reserved for the sample for analysis; any loose sand or other deleterious matter on the reserved portions shall be removed, conveniently by brushing.

The sample for analysis shall be collected, after the proper discard, by drilling each pig or portion of pig with a properly sharpened and hardened, flat-bead,  $\frac{5}{8}$ - or  $\frac{3}{4}$ -in. high-speed tool-steel drill, in a direction at right angles to the long axis of the pig, and at such a feed as to form a minimum amount of fine drillings. The first drillings shall be discarded, and only the drillings collected after the drill has penetrated  $\frac{1}{4}$  in. shall be reserved for the sample. The drilling shall extend to within  $\frac{1}{4}$  in. of the opposite surface of the pig. Suitable precautions shall be taken to collect all the drillings, fine as well as coarse particles, and to avoid contamination of the sample in any way. Any pigs or portions of pigs found too hard to drill readily may be annealed by heating to a dark red color and cooling in air.

The sample for analysis shall be composed of equal portions by weight of the drillings from the pigs forming the unit sample. The weight of the combined sample shall be not less than 75 g. The drillings shall be thoroughly mixed, as by gently grinding in a suitable mortar until all pass the No. 20 (840- $\mu$ ) sieve. Unless accurate determinations of combined and graphitic carbon are required, the



sample shall be carefully divided into three equal parts in accordance with Section f., p. 649.

When combined and graphitic carbon must be determined with the highest degree of accuracy, equal portions by weight of the drillings from the pigs or parts of pigs representing a unit sample shall be mixed to form a sample of at least 100 g., which shall then be separated into coarse and fines by sieving as described in the following section.

### c. GRAY IRON CASTINGS

In accordance with the Specifications for Gray Iron Castings (ASTM Designation: A48),<sup>4</sup> three test bars 1.20 in. in diameter shall be cast in sand from each heat after one-fourth and after three-fourths of the heat has been poured. One bar from each set shall be broken. One end of each, next to the fracture, shall be thoroughly cleaned and the outer skin removed for a sufficient distance from the fracture, down to clean metal. Chips shall then be taken by means of a lathe or milling machine across the whole face of the bar, until not less than 100 g. have been collected. The same amount shall be taken from each bar. The bar shall be so clamped as to permit the attachment or use of any suitable device for collecting every part of the sample, and the machine shall be run slowly enough to reduce to a minimum the danger of loss of fine particles (avoid drafts). Horizontal drilling may also be employed.

The entire gross sample shall be weighed and then sifted on a No. 80 (177- $\mu$ ) and, if necessary, a No. 120 (125- $\mu$ ) sieve with cover. Both sieves and cover must be tight-fitting to avoid loss of fine graphite by dusting. As an alternative procedure: (1) the drillings may be sifted through two sieves of such sizes that not under 10% nor over 20% of the entire sample remains on the larger sieve, and not under 10% nor over 20% passes through the smaller sieve; or (2) sieves may be used of such sizes that concordant results may be obtained. The two (or three) portions so obtained shall be separately weighed. Each one shall then be thoroughly mixed without any loss of material, and then divided into three parts in accordance with Section f., p. 649. Before weighing the sample for analysis, the contents of each bottle shall be thoroughly mixed. Carbon is determined on each of the sieved portions, and the carbon present in the original drillings is calculated from the ratio of the weights of the separate sieved fractions to the original iron. As a general rule, the very fine material is richest in carbon, the coarse material next, while the intermediate sizes are the poorest.

For routine analyses, the aim should be to obtain the iron in as small particles as possible, as for example by milling. In such case, the samples for graphite and carbon may be taken by forming a cone, flattening it out, and taking small dabs with a spatula from at least ten representative portions for each weighed portion. Less care is needed in taking portions for the determination of the other constituents; grab samples from the container after gentle tumbling are satisfactory.

### d. MALLEABLE IRON

Malleable iron shall be sampled in the same manner as described for pig iron.

### e. WROUGHT IRON

As it is desirable that the sample represent the entire cross-section of the specimen, sampling by milling is preferable. Specimens shall be freed from any mill

<sup>4</sup> 1960 Supplement to Book of ASTM Standards, Part 1.

scale by pickling, grinding, or other suitable means. It is necessary to secure all of the millings, for the various sized particles will differ in composition. For routine work, samples for carbon, manganese, phosphorus, sulfur, and silicon may be taken from the thoroughly mixed millings. For the determination of slag and oxides, or for umpire determinations of the other constituents, the entire sample shall be weighed and then sifted without dusting on a No. 35 (500- $\mu$ ) sieve. The two fractions shall be weighed, and in taking samples for analysis, portions of these two well mixed fractions shall be taken in the same proportion that they bear to the gross sample.

#### f. SIZE OF SAMPLE AND STORAGE

The prepared sample shall weigh at least 100 g. The sample, or each fraction into which it has been separated by sieving (Section c), shall be divided into three equal parts, each of which shall be placed in a sealed package, one for the manufacturer, one for the purchaser, and one for an umpire, if necessary. Samples that are to be stored over long periods, or that are oxidized readily, or otherwise altered in composition under varying atmospheric conditions, or that may become seriously contaminated in contact with paper or cardboard, should be kept in wide-mouth glass bottles of approximately 2-oz. capacity, having tightly fitting screw caps of metal or preferably, plastic composition. In other cases, tight, leak-proof, paper sample envelopes or cardboard cartons may be used to hold the sample.

#### g. RESAMPLING

In the case of dissatisfaction or disagreement, the metal shall be resampled in the presence of representatives of the manufacturer and the purchaser. The thoroughly mixed samples shall be divided into three equal parts, each of which shall be placed in a sealed package, one for the manufacturer, one for the purchaser, and one for an umpire, if necessary.

### WATER, REAGENTS, AND GLASSWARE

*Water.*—Unless otherwise indicated, references to water shall be understood to mean distilled water or other water of equivalent purity.<sup>5</sup>

*Reagents. Purity.*—Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available.<sup>6</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. In addition to this, it is desirable in many cases for the analyst to assure the accuracy of his results by running blanks or checking against a comparable sample of known composition.

*Concentrated Acids, Ammonium Hydroxide, and Hydrogen Peroxide.*—When acids, ammonium hydroxide, and hydrogen peroxide are specified by name or

<sup>5</sup> Water conforming to the Specifications for Reagent Water (ASTM Designation: D1193), 1958 Book of ASTM Standards, Parts 6 to 10, meets these requirements.

<sup>6</sup> Reagent Chemicals, American Chemical Society Specifications, Am. Chem. Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see Rosin, Joseph, Reagent Chemicals and Standards, 4th Ed., D. Van Nostrand Co., Inc., Princeton, N. J., 1961, and the United States Pharmacopeia.

chemical formula only, it shall be understood that concentrated reagents of the specific gravities or concentrations shown in Table 24-1 are intended. The desired specific gravities or concentrations of all other concentrated acids shall be stated wherever they are specified.

TABLE 24-1. CONCENTRATIONS OF ACIDS, AMMONIUM HYDROXIDE, AND HYDROGEN PEROXIDE

Name	Formula	Specific Gravity, approx.	Percentage of Reagent by Weight		
			Nominal	Min.	Max.
Acetic acid .....	$\text{CH}_3\text{COOH}$	1.05	...	99.5	...
Formic acid.....	$\text{HCOOH}$	1.20	...	88	...
Hydrobromic acid ...	$\text{HBr}$	1.49	48	47.0	49.0
Hydrochloric acid.....	$\text{HCl}$	1.19	...	35.0	38.0
Hydrofluoric acid. ...	$\text{HF}$	1.15	...	48.0	51.0
Nitric acid.....	$\text{HNO}_3$	1.42	...	69.0	71.0
Perchloric acid .....	$\text{HClO}_4$	1.67	...	70.0	72.0
Phosphoric acid . ...	$\text{H}_3\text{PO}_4$	1.69	...	85	...
Sulfuric acid .. ...	$\text{H}_2\text{SO}_4$	1.84	...	95.0	98.0
Sulfurous acid ..	$\text{H}_2\text{SO}_3$	1.03	...	6 ( $\text{SO}_2$ )	...
Ammonium hydroxide	$\text{NH}_4\text{OH}$	0.90	...	27.0 ( $\text{NH}_3$ )	30.0 ( $\text{NH}_3$ )
Hydrogen peroxide .	$\text{H}_2\text{O}_2$	1.10	30	28	...

**Diluted Acids and Ammonium Hydroxide.**—Concentrations of diluted acids and ammonium hydroxide, except when standardized, shall be specified as a ratio stating the number of volumes of the concentrated reagent to be diluted with a given number of volumes of water, as in the following example:  $\text{HCl}$  (5:95) means 5 volumes of concentrated  $\text{HCl}$  (sp. gr. 1.19) diluted with 95 volumes of water.

**Standard Solutions.**—Concentrations of standard solutions shall be expressed as normalities or as equivalents in grams per milliliter of the element to be determined, for example: 0.1 N  $\text{KMnO}_4$ , or  $\text{Na}_2\text{S}_2\text{O}_3$  (1 ml. = 0.0006 g. Cu).

**Nonstandardized Solutions.**—Concentrations of nonstandardized solutions prepared by dissolving a given weight of the solid reagent in a solvent shall be specified in grams of the salt as weighed out per liter of solution, and it shall be understood that water is the solvent unless otherwise specified, for example: to prepare barium chloride solution (100 g. per liter) dissolve 100 g. of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in water and dilute to 1 liter. In the case of certain reagents, the concentration may be specified as a percentage by weight, for example:  $\text{H}_2\text{O}_2$  (3%) means a solution containing 3 g. of  $\text{H}_2\text{O}_2$  per 100 g. of solution. Other nonstandardized solutions may be specified by name only and the concentration of such solutions will be governed by the instructions for their preparation.

<sup>7</sup> In a number of the methods, the concentrations of nonstandardized reagents are now given in terms of grams of anhydrous salt per liter of solution, as clearly indicated in their descriptions. When the methods are next extensively revised, the descriptions of the reagents will be revised to conform with Section 4(d) of E50.

**Glassware.**<sup>8</sup>—All glass apparatus and vessels used in analytical work should be carefully selected to meet the particular requirements for each operation. Standard volumetric flasks, burets, and pipets should be of precision grade. New and improved types of glass apparatus are available, including colored glass for the protection of solutions affected by light, alkali-resistant glass for use where superior resistance to alkalis is important, and a high-silica glass having exceptional resistance to thermal shock. Standard-taper, interchangeable, ground-glass joints are very useful in analytical work.

**Safety Precautions.**—The analytical worker should be conscious of, and ready to guard against, hazardous chemical operations, which may have deleterious physiological effects or carry the risk of explosion, fire, etc.<sup>9</sup> The corrosive and injurious nature of concentrated acids, alkalis, and the like is generally understood. The poisonous nature of cyanides and hydrocyanic acid calls for care in handling burets and other vessels that are used in working with them. The importance of wearing protective goggles while performing distillations, fusions with peroxide, and other similar operations cannot be overemphasized. Suitable gas masks should be worn when handling cylinders of poisonous gases, or in other operations that may lead to the accidental liberation of a high concentration of poisonous gas. An air-fed helmet supplied from a compressed air line should be provided in any closed room where a cylinder of a poisonous gas is to be attached to a supply line. Cylinders should be chained to a suitable support before the shipping caps are removed. Adequate, properly ventilated storage space should be provided for hazardous chemicals; such storage, for most laboratories, should be provided in a separate structure. Hazards and precautions applying to eight specific materials are covered in the following paragraphs.

**Beryllium.**—Beryllium and its compounds offer a serious health hazard. The use of precautions against dusting and spraying of compounds or solutions is imperative. The transfer of dry powders must be done in a "dry box" with attachment to a filter system connected to a gentle vacuum line.

**Radioactive Materials.**—These offer special hazards that call for special training and special health protection. For high levels of activity, special construction is essential, and provision for proper disposal of radioactive wastes must be made.

**Hydrofluoric Acid.**—Hydrofluoric acid burns are both painful and dangerous, as infection and necrosis of bone tissue may occur. Even if only one drop of HF has touched the skin, wash immediately with plenty of water, and soak the exposed part in a strong solution of borax.

<sup>8</sup> For further information the following references may be consulted: Tentative Method of Testing and Standardization of Etched-Stem Liquid-in-Glass Thermometers (ASTM Designation: E77), 1958 Book of ASTM Standards, Part 7; Hughes, J. C., Testing of Hydrometers, Nat. Bureau Standards Circular 555, U. S. Government Printing Office, Washington, D. C., 1954; Moran, J. J., Methods of Testing Volumetric Glassware, Proceedings, ASTM, 41, 492, 1941; Peffer, E. L., and Mulligan, G. C., Testing of Glass Volumetric Apparatus, Nat. Bureau Standards Circular C434, U. S. Government Printing Office, Washington, D. C., 1941.

<sup>9</sup> For a summary of health hazards, the following references may be consulted: Van Arsdell, P. M., Health Hazards of Common Laboratory Reagents, Chemical and Engineering News, 26, 304, February 2, 1948; Patty, F. A., Industrial Hygiene and Toxicology, 2 vols., Interscience Publishers, Inc., New York, 1949; Sax, N. I., Dangerous Properties of Industrial Materials, Reinhold Publishing Corp., New York, 1957; General Safety Committee of the Manufacturing Chemists' Association, Inc., Guide for Safety in the Chemical Laboratory, D. Van Nostrand Co., Inc., Princeton, N. J., 1954.

**Nitric Oxide.**—These vapors are cumulatively harmful to the respiratory system, so solution of metals in  $\text{HNO}_3$  should be made in a well-ventilated hood.

**Hydrogen Sulfide.**—Whenever possible, the generation of  $\text{H}_2\text{S}$  should be limited to the amounts needed for the work at hand. The gas should be used only under an adequate hood, since it is more toxic than cyanide. When cylinders and storage tanks are used, it is desirable that the cylinder and tank be housed under cover with free access of air. The use of a helmet, furnished with a compressed air connection, is desirable when changing cylinders or making repairs. Fatal accidents have resulted from loosening the nut of the purge vent instead of the nut leading from the valve.

**Organic Solvents.**—Regard all organic solvents as harmful, and avoid inhaling small amounts of vapor on repeated occasions. Smoking or open flames should be prohibited in areas where organic solvents are in use or in storage.

**Metallic Mercury.**—Metallic mercury gives off an appreciable amount of vapor; it must not be handled in quantity in a confined space, even at room temperature. Every effort should be made to avoid spilling mercury since it easily lodges in cracks and crevices and may result in mercury poisoning.

**Perchloric Acid.**—This acid has many desirable analytical uses that can be safely practiced with proper precautions. The well diluted acid has no hazardous properties, but the hot, concentrated, constant-boiling acid in contact with reducing matter, organic or inorganic, may produce violent and dangerous explosions. Precautions that should be taken in using  $\text{HClO}_4$  are as follows:<sup>10</sup>

**Storage.**—Perchloric acid is normally purchased as either a 60 or 70% solution. This acid should be stored away from flammable and reducing materials, in a room or building that has ceramic floors, sides, and walls. If the acid becomes colored while standing, discard it immediately. There should be provision for flushing any spilled acid from broken containers, etc., down a drain, using adequate water to maintain proper dilution.

**Hoods.**—For fuming operations with the constant-boiling acid for the determination of silica, and like operations, it is imperative that the condensed acid fumes do not come into contact with wood or other reducing material. The ideal bench and hood would consist of nonabsorbing, acid-resistant material with provision for washing down the exhaust flue and interior of the hood once a month or oftener. Such hoods are commercially available, and should be considered in planning new installations or in redesigning old ones. Only inorganic cements should be used in joining the sections of the hood and bench. Litharge-glycerine cement should not be used in any part of a laboratory using  $\text{HClO}_4$ . A hot crucible placed on such a joint may cause a violent explosion if  $\text{HClO}_4$  has previously been spilled and absorbed in the litharge glycerine joint. The washing operation should be done in such a way that the condensed acid is greatly diluted. Protective clothing is desirable. If tools must be used in connection with cleaning, they should be used only after thorough water dilution of the acid; nonsparking materials, such as wood, hard rubber mallets, or fiber brushes, should be used.

<sup>10</sup> For additional information on precautions for the use of  $\text{HClO}_4$ , reference may be made to the following: Chemical Safety Data Sheet SD-11, Perchloric Acid Solution, Manufacturing Chemists' Association, Inc., Washington, D. C., 1947; Perchloric Acid Data Sheet D-311 (D-Chem 44), National Safety Council, Chicago; Sax, N. I., *Dangerous Properties of Industrial Materials*, Reinhold Publishing Corp., New York, 1957; General Safety Committee of the Manufacturing Chemists' Association, Inc., *Guide for Safety in the Chemical Laboratory*, D Van Nostrand Co., Inc., Princeton, N. J., 1954.

*Destruction of Organic Matter.*—Evaporation of organic solvents or ignitions of combustible material should be prohibited in hoods that are used for work with  $\text{HClO}_4$ . Filter papers that are used to filter solutions of dilute  $\text{HClO}_4$  may, if insufficiently washed, deflagrate or explode during drying. Solutions of perchlorates and acids, or of  $\text{HClO}_4$  in organic solvents, are hazardous mixtures and should never be heated or agitated violently. *Under no circumstances should a mixture containing  $\text{HClO}_4$  and alcohol be heated or evaporated;* some of the most dangerous and damaging explosions have resulted from neglect of this rule. Perchloric acid is often used to destroy the last traces of organic matter in analytical operations. The bulk of the organic matter is destroyed by repeated evaporations with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , followed by dilution after cooling, and addition of minimal amounts of  $\text{HClO}_4$ , followed by further heating. This process, if improperly carried out, that is, by adding  $\text{HClO}_4$  while there is an appreciable quantity of organic matter and the  $\text{H}_2\text{SO}_4$  is concentrated, may lead to violent explosions.<sup>11</sup>

*Drying Operations.*—Magnesium perchlorate, which is used as a drying agent, should not be used in the presence of strong acid or of organic matter. Serious explosions have resulted from its use for drying an organic liquid that has been in contact with sulfuric acid and has been poorly washed.<sup>12</sup> It has been reported that if  $\text{Mg}(\text{ClO}_4)_2$  is allowed to absorb  $\text{NH}_3$  gas, an explosion may result.<sup>13</sup>

*Metals and Alloys.*—Hot, concentrated  $\text{HClO}_4$  may react with finely divided metals to give violent explosions. Metallic antimony or bismuth has caused explosions.<sup>14</sup> In general, the contact of hot, concentrated  $\text{HClO}_4$  with any strongly reducing material is hazardous. W. Dietz<sup>15</sup> has reported an explosion when steel was being dissolved. The explosion was presumed to have been caused by the action of the hot  $\text{HClO}_4$  vapor on the hydrogen simultaneously evolved. Dilution of the  $\text{HClO}_4$  tends to minimize the explosion hazard. *Nitric acid should always be used with  $\text{HClO}_4$  when metals and alloys are being dissolved.* In this way  $\text{HNO}_3$  serves as the major oxidizing agent, and lowers the  $\text{HClO}_4$  concentration, so that by the time  $\text{HClO}_4$  boils, the possibility of a violent explosion is minimized.

<sup>11</sup> For information on explosion hazards, refer to the following: Kahane, E., Explosion Hazards in the Use of Perchloric Acid, Comptes rendus, Seventeenth Congress of the Chemical Industry in Paris, 1937, p. 471; Chemical Abstracts, 32, 6463, 1938 (For safety, the bulk of the organic matter is destroyed by nitric acid, and the perchloric acid is added to sufficient cold dilute solution.); Kahane, E., Über Unfälle bei der Zerstörung organischer und Überchorsäure, Zeitschrift für analytische Chemie, 111, 14, 1937; Balks, R., and Wehrmann, O., A Warning Against the Use of Perchloric Acid Mixtures for the Decomposition of Animal Substances, Bodenkunde und Pflanzenernähr, 11, 253, 1938; Chemical Abstracts, 33, 2438, 1939 (Some forms of animal material are insufficiently decomposed by  $\text{HNO}_3$  to permit final use of  $\text{HClO}_4$ ); Kahane, E., Comptes rendus, 193, 1018, 1931; Chemical Abstracts, 26, 940, 1932; Smith, G. F., Perchloric Acid, 3rd Ed., The G. Frederick Smith Chemical Co., Columbus, Ohio, 1934; Smith, G. F., The Wet Ashing of Organic Matter Employing Hot Concentrated Perchloric Acid—The Liquid Fire Reaction, Anal. Chim. Acta, 8, 397, 1953; Smith, G. F., The Dualistic and Versatile Reaction Properties of Perchloric Acid, Analyst, 80, 16, 1955.

<sup>12</sup> Pieters, H. A. J., with the collaboration of Creighton, J. W., Safety in the Chemical Laboratory, Academic Press, Inc., New York, 27, 1951.

<sup>13</sup> Private communication from G. Frederick Smith.

<sup>14</sup> Fichter, F., and Jenny, E., Perchlorates of Bismuth and Antimony, Helvetica Chimica Acta, 6, 225, 1923; Chemical Abstracts, 17, 1599, 1923.

<sup>15</sup> Dietz, W., Über die Ungefährlichkeit konstant siedender, 72 prozentiger Überchorsäure, Angewandte Chemie, 52, 616, 1939.

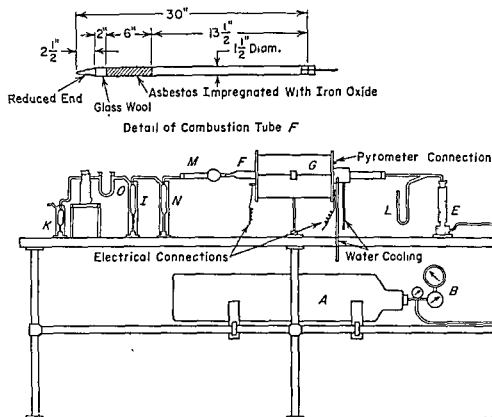


FIG. 24-2. Typical Arrangement for Determination of Carbon by the Direct-Combustion Method: *A*, a 100-cu. ft. cylinder of oxygen; *B*, reducing valve; *C*, rubber tubing; *E*, tower containing soda lime for removing any  $\text{CO}_2$  in the oxygen. A layer of about  $\frac{1}{2}$  in. of anhydrous  $\text{Mg}(\text{ClO}_4)_2$  is placed on top for removing traces of moisture; *F*, combustion tube. The asbestos impregnated with iron oxide is prepared by treating some asbestos with a saturated solution of  $\text{Fe}(\text{NO}_3)_3$ , drying and heating to  $1000^\circ\text{C}$ . The treated asbestos is placed lightly in the combustion tube, and not packed; *G*, electric furnace; *L*, manometer gauge; *M*, glass tube lightly packed with absorbent cotton to remove solid particles; *N*, bottle containing 25 ml. of  $\text{H}_2\text{SO}_4$  (1.4) saturated with chromic acid to remove sulfur gases from the gas stream; *I*, bottle contains 50 ml. of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) for removing the bulk of the moisture that passes over from bottle *N*. Where a large number of carbon determinations are being made the acid in this bottle should be changed daily. *O*, U-tube containing anhydrous  $\text{Mg}(\text{ClO}_4)_2$ ; this tube is filled lightly and evenly, so as not to cause packing; *J*, absorbing bulb containing a 20- to 30-mesh inert base impregnated with  $\text{NaOH}$ , for absorbing the  $\text{CO}_2$ . A layer of glass wool is placed in the bottom and top of the bulb, and the soda-impregnated  $\text{CO}_2$  absorbent is covered with a layer of anhydrous  $\text{Mg}(\text{ClO}_4)_2$  approximately  $\frac{1}{2}$  in. in thickness; *K*, bottle containing  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84); may be omitted if the stopcock in *J* is so manipulated during combustion that no air is drawn through the exit tube.

## TOTAL CARBON BY THE DIRECT-COMBUSTION METHOD

**Apparatus and Reagents.**—The apparatus shall be suitable for the direct combustion of the metal in oxygen, with the  $\text{CO}_2$  obtained being collected in a suitable adsorbent, consisting of an inert base impregnated with  $\text{NaOH}$ <sup>16</sup> and with suitable purifying and protecting trains following the furnace. Figures 24-2 and 24-3 show two typical arrangements of the apparatus. The apparatus and arrangement may be modified, provided satisfactory results for the carbon determination will be ob-

<sup>16</sup> Ascarite and Caroxite have been found satisfactory for this purpose.

tained. Owing to the diversity of apparatus by which correct results may be obtained in the determination of carbon, the recommendations given in the following paragraphs are intended to indicate what is acceptable, rather than to prescribe definitely what shall be used.

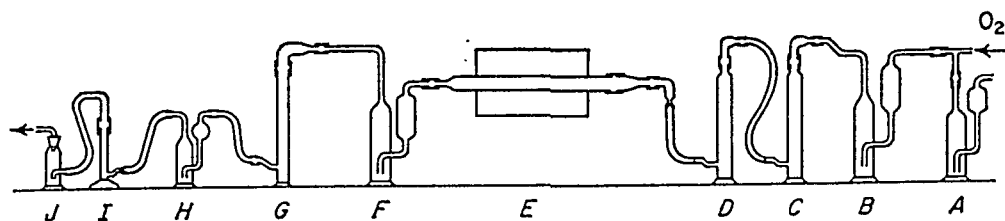


FIG. 24-3. Typical Arrangement for Determination of Carbon by the Direct-Combustion Method: *A*, mercury valve; *B*, bottle containing concentrated  $\text{H}_2\text{SO}_4$ ; *C*, tower, with goose-neck top, containing  $\text{CaCl}_2$ ; *D*, tower containing stick  $\text{NaOH}$ ; *E*, electric furnace with combustion tube and adapters; *F*, bottle containing  $\text{KMnO}_4$  (50 g. per l.), inserted only for steels with over 0.05% sulfur; *G*, tower containing granulated zinc; *H*, bottle containing concentrated  $\text{H}_2\text{SO}_4$ ; *I*, tower containing  $\text{P}_2\text{O}_5$ ; *J*, weighed tower containing a 20- to 30-mesh inert base impregnated with  $\text{NaOH}$ , for absorbing the  $\text{CO}_2$ .

**Combustion Apparatus.**—Any combustion apparatus (preferably heated by electricity) that will heat the sample to a temperature of  $1000^\circ$  to  $1100^\circ\text{C}$ . may be used for carbon steels and most low-alloy steels. Electric furnaces heated by silicon carbide rods, giving temperatures up to  $1400^\circ\text{C}$ ., are very useful for determining carbon in refractory alloys. Combustion tubes may be of porcelain, sillimanite, clay, quartz, or platinum, and must be gastight. Quartz is liable to devitrification when used intermittently at temperatures above  $1000^\circ\text{C}$ ., and may then become porous. Tubes 30 in. long and  $1\frac{1}{4}$  in. I.D., and drawn out at one end, may be used conveniently for the small Gooch crucibles of fused silica that are used in the determination of graphite in cast iron.

**Catalyzers.**—Though materials such as ironized asbestos, copper oxide, platinized quartz or asbestos, or platinum gauze are often put in the exit end of the combustion tube for the purpose of insuring complete combustion of carbon to  $\text{CO}_2$ , it is questionable whether they are of any value, except to serve as baffles for holding back finely divided solid metallic oxides and sulfur trioxide, since they soon become fouled. When such baffles are used, the fixed sulfur shall be burned out every 200 determinations or oftener by drawing the exit end of the combustion tube into the hot zone, while a current of air or oxygen is passed through it. When carbon determinations are being made on materials with high sulfur contents, baffles should not be used in the exit end of the tube, but a special  $\text{SO}_2$  absorber or purifier should be placed between the tube and the  $\text{CO}_2$  absorber.

**Boats and Covers.**—The boats and covers may be of alundum, clay, zirkite, nickel, or platinum, and should preferably receive a lining of granular alundum or other material found to be suitable for the purpose. Nickel boats shall be made of sheet nickel containing under 0.10% of carbon. Before use, new boats and covers shall always be preheated in oxygen until no more  $\text{CO}_2$  is given off, or until a constant blank is obtained. In order to prevent injury to the tube from spattering, a platinum or nickel cover, open at both ends, and allowing free access of oxygen, should be used.



**Material for Lining Boats.**—Granular alundum,<sup>17</sup> alkali-free, 60-mesh or finer, specially prepared for carbon determinations, is entirely satisfactory for the lining of boats. Ignited low-silica chrome ore, or zirkite (natural oxide of zirconium), properly sized and freed from materials causing a blank may be employed. Ferric oxide is recommended as permitting combustion of carbon steels at low temperatures (800° to 900°C.), but is not recommended for high temperatures. Quartz sand is objectionable, owing to its liability to fuse or to slag with oxides of iron, causing bubbles of gas to be enclosed.

**Absorbing Bulbs.**—No special types of absorbing bulbs are recommended, although the Fleming, Miller, Turner, and the Midvale (sometimes called Stetzer and Norton) bulbs have proved satisfactory. When filled, the tubes shall not weigh over 200 g., and they shall always be weighed, filled with oxygen, against a like counterpoise. Open bulbs, such as the Midvale, lose oxygen by diffusion. They shall be filled with oxygen before weighing, when not in continuous use, and the same time interval shall be held between weighings.

**Oxygen Purifiers.**—The purity of the oxygen shall be not less than 99.5%. Organic matter of any kind is an undesirable impurity. It is usually absent, and it suffices to pass the oxygen through an absorbent such as a 20- to 30-mesh inert base impregnated with NaOH, followed by anhydrous  $Mg(ClO_4)_2$ . If carbonaceous matter is suspected, the oxygen shall be passed through a tube that is loosely packed with copper oxide and heated to about 450°C. before it is passed through the NaOH-impregnated material.

**Carbon Dioxide Purifiers.**—The purifiers that follow the combustion tube must remove finely divided solid metallic oxides and oxides of sulfur or selenium, dry the gases before they enter the weighed  $CO_2$  absorber, and protect the absorber from outside effects. Finely divided solid metallic oxides are removed from the gases during their passage through the liquids or columns of solids that precede the weighed absorber. The small amounts of  $SO_2$  that are given off from materials low in sulfur may be satisfactorily removed by  $H_2SO_4$  that has been saturated with chromic acid. Materials with high sulfur contents need other absorbents such as chromic acid (500 g. per liter) or  $KMnO_4$  (50 g. per liter), followed by suitable desiccants, or heated platinized silica gel, that will convert the  $SO_2$  to  $SO_3$ . The  $SO_3$  that is so formed is not removed by any one absorbent, but is condensed and absorbed during its passage through the liquids or columns of solids in the train. An asbestos or glass-wool filter should be used after such absorbents as the chromic acid solution to prevent the spray from coming in contact with rubber connections, thus causing high values to be obtained. A tube containing a mixture of ironized asbestos and anhydrous  $Mg(ClO_4)_2$  should be used after the platinized silica gel. The ironized asbestos should be prepared as follows: saturate 20 g. of long-fiber asbestos with a saturated solution of  $Fe(NO_3)_3$ , dry, and ignite at 1000°C.

**Carbon Dioxide Absorbents.**—The most desirable absorbent for  $CO_2$  is 20- to 30-mesh inert base impregnated with NaOH, followed by anhydrous  $Mg(ClO_4)_2$  at the exit end. The latter is needed to absorb the water that is formed during the reaction and is not held by the unused  $CO_2$  absorbent.

**Procedure.** Carbon and High-Silicon Steels Containing Under 0.1% Sulfur.—After having properly set up and tested the apparatus, spread 1 to 5 g. of the sample on the bed material in the boat so that the particles are in intimate contact.<sup>18</sup>

<sup>17</sup> R. R. Alundum has been found satisfactory for this purpose.

<sup>18</sup> In general, the sample shall be packed in a small groove or furrow that has been made in the bedding material in the boat. If the material burns too rapidly, satisfactory

Cover the sample with a suitable cover and introduce the boat into the hot combustion tube. Close the tube and allow the sample to heat for 1 to 2 min.,<sup>19</sup> depending upon the size of the particles.<sup>20</sup> Then admit oxygen<sup>21</sup> at a rate of 800 to 1000 ml. per min. while combustion is going on.<sup>22</sup> Use a furnace temperature of 1100°C. or above. When combustion is complete (1.5 to 2 min.), reduce the rate of flow of oxygen to 400 to 500 ml. per min. and continue for 6 to 8 min. in order to sweep out the CO<sub>2</sub>. Withdraw the absorption tube filled with oxygen, place it in the balance case for 10 min.,<sup>23</sup> open momentarily, and weigh against a similar tube used as a counterpoise. The increase in weight represents CO<sub>2</sub>. Remove the boat from the tube and examine the fusion for evidences of incomplete combustion. If the drillings are not thoroughly fused in a solid pig, the determination shall be rejected.

Make a blank determination, following the same procedure and using the same amounts of all materials except the sample. Calculate the percentage of carbon as follows:

$$\text{Carbon, per cent} = \frac{(A - B) \times 0.2729}{C} \times 100$$

where  $A$  = grams of CO<sub>2</sub>,

$B$  = correction for blank, in grams, and

$C$  = grams of sample used.

**High-Sulfur Steels.**—Determine carbon in accordance with the procedure described above, but insert a special SO<sub>2</sub> oxidant in the train consisting of a tube of platinized silica gel heated to 440°C., followed by a tube containing ironized asbestos (see Figs. 24-2 and 24-3) and anhydrous Mg(ClO<sub>4</sub>)<sub>2</sub>.

**Alloy Steels.**—Determine carbon in accordance with the procedure described in the section on carbon and high-silicon steels, above. Although most of the low-alloy steels burn perfectly at 1100°C. without the addition of an accelerator, many alloy steels require an accelerator to obtain complete combustion at this temperature. If a steel burns with difficulty, either place a small (1/8 in.) pellet of tin on

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regulation of the speed of combustion may sometimes be obtained by spreading the sample somewhat loosely over the bedding material or by covering with a thin layer of the bedding material or, preferably, ignited CuO.

<sup>19</sup> If the sample is allowed to come to the temperature of the furnace before the oxygen is admitted, it usually bursts into a bright flame and burns completely. A period of 1 to 2 min. of preheating suffices.

<sup>20</sup> The finer the chips (excluding dust, which causes low values on a hot boat) the better, except with alloys that burn too vigorously. Drillings or millings sized between 14 and 60 mesh are satisfactory.

<sup>21</sup> "Hospital grade" oxygen is preferred for this purpose.

<sup>22</sup> The rate at which oxygen is admitted is also a factor in the velocity of combustion. Assuming the combustion apparatus has been heated to the temperature range above that recommended, it is possible, if the material is closely packed, and if oxygen is admitted at too rapid a rate, that the combustion may be so violent as to cause excessive spattering of fused oxides and such fluidity of the molten slag that the boat or other container may be injured or destroyed. Sufficient oxygen, however, shall be run in to insure a current of gas through the absorber at all stages of the combustion. When tin is employed as an accelerator, combustion is very rapid and it is, therefore, necessary to increase the flow of oxygen during combustion.

<sup>23</sup> The tube will warm up when CO<sub>2</sub> is absorbed. It is not necessary to wait until it reaches room temperature if it is in continuous use, provided the same time interval is maintained, and approximately the same amount of CO<sub>2</sub> is absorbed.

each end of the sample (or spread 1 g. of tin millings over the sample) or mix with 1 to 2 g. of 40-mesh millings of open-hearth iron, and proceed as usual.<sup>24</sup>

With high-chromium, high-nickel steels (18% chromium, 8% nickel; 20% chromium, 20% nickel; etc.), the principal sources of error in carbon determinations are: (1) combustion at too low temperatures; and (2) omission of, or faulty corrections for, blank determinations. More certain combustion of all carbon is obtained if a temperature of 1250°C. or higher is employed and tin or open-hearth iron is used as an accelerator. Preheating is necessary,<sup>19</sup> and burning at higher pressures of oxygen seems advantageous; that is, a sufficiently rapid stream of oxygen should be maintained during the burning so that it is bubbling freely at the exit end of the train. After the burning is completed, continue the flow of oxygen for 6 to 8 min. in order to sweep out the CO<sub>2</sub>. If sulfur exceeds 0.06%, special precautions shall be taken to eliminate oxides of sulfur. Steels containing boron require a higher temperature than 1100° to 1150°C., if tin is used as the accelerator. This temperature is satisfactory if pure iron is used as the flux.

**Selenium Steels.**—Determine carbon as described for high-sulfur steels above.

**Pig Iron, Cast Iron, and Malleable Iron.**—Determine carbon in accordance with the procedure described for carbon and high-silicon steels, using 1 g. of the sample. Special care shall be used in obtaining a representative sample (see Sections b, c and d above, on sampling). Precautions for sulfur are of no particular moment for cast iron, except, of course, for continuous combustions of iron containing more than 0.10% of sulfur.

**Procedure for Alloy Cast Iron.**—Determine carbon in accordance with the procedure described for carbon and high-silicon steels. High-silicon and most alloy cast irons require a temperature of at least 1100°C. for complete combustion. Accelerators (see the section on alloy steels) are desirable for high-chromium, high-nickel iron.

**Open-Hearth Iron and Wrought Iron.**—Determine carbon in accordance with the procedure described for carbon and high-silicon steels, using 3 to 4 g. of the sample, and paying special attention to proper blank corrections. With very low-carbon material, as open-hearth iron, the use of small absorption tubes<sup>25</sup> tends to reduce errors caused by variations in temperature and humidity.

**Graphite in Cast Iron.**—Transfer 1 to 3 g. of the sample to a 250-ml. beaker. Add 50 ml. of HNO<sub>3</sub> (3:5), cover, and heat on a steam bath for about 30 min., while stirring occasionally. Add 1 to 2 ml. of HF and boil gently for 4 to 5 min. Collect the residue, conveniently by suction on ignited asbestos contained in a fused-silica Gooch crucible of such diameter as will fit in the combustion tube. Wash thoroughly with hot water, hot KOH (120 g. per liter), hot water, HCl (1:20),

<sup>24</sup> Red lead, copper oxide, lead, and powdered copper are also used as accelerators. Red lead to be used for this purpose should first be heated in an atmosphere of oxygen in an open porcelain dish, with frequent stirring, at 500° to 550°C. for 15 to 24 hr., then cooled in a desiccator and transferred to a tightly stoppered bottle, preferably one with a ground-glass stopper. When red lead is employed, the determination should be completed promptly, in order not to expose the red lead to the atmosphere any longer than necessary, as it readily absorbs CO<sub>2</sub> from the air. With high-silicon alloys known to contain silicon carbide, it is necessary to use red lead only when the temperature of the furnace is approximately 1100°C. When a furnace temperature of 1350°C. or higher is used, all of the carbon can be obtained by mixing the sample with an equal weight of CuO and burning with the weight of ingot iron millings or drillings specified.

<sup>25</sup> Schwartz glass-stoppered, 10-cm., U-shaped absorption tubes containing a CO<sub>2</sub> absorbent such as inert base impregnated with NaOH, and anhydrous Mg(ClO<sub>4</sub>)<sub>2</sub>, are satisfactory for this purpose.

and hot water, in the order given. Dry the residue at a temperature not exceeding 150°C., and determine the graphite by direct combustion at 1000°C. in the apparatus used for the determination of total carbon.

## MANGANESE

### THE BISMUTHATE METHOD (ABSENCE OF COBALT)

**Apparatus.** Filter.—A Gooch crucible or a fritted-glass or alundum filtering funnel of the Büchner type, of sufficiently fine porosity to prevent passage of bismuthate particles.

**Reagents.** (a) **Sodium Bismuthate.**—The sodium bismuthate shall contain enough active oxygen to correspond to at least 75%  $\text{NaBiO}_3$ . Manganese and chlorides shall not exceed 0.005 and 0.001%, respectively.

(b) **Sulfurous Acid.**—Saturate water with  $\text{SO}_2$ . Prepare fresh as required.

(c) **Nitric Acid (3:97).**

(d) **Ferrous Ammonium Sulfate Solution.**—Dissolve 12 g. of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  in cold  $\text{H}_2\text{SO}_4$  (1:19).

(e) **Standard Potassium Permanganate Solution (0.03 N).**

(f) **Standard Sodium Arsenite Solution (1 ml. = 0.0007 g. Mn).**—The solution is preferably standardized against a standard steel of approximately the same manganese content as the sample, except for open-hearth iron and wrought iron. For open-hearth iron and wrought iron, standardize as follows: dissolve 1 g. of electrolytic or open-hearth iron of a known, low manganese content<sup>26</sup> in 30 ml. of  $\text{HNO}_3$  (1:2). Add exactly 20 ml. of 0.03 N  $\text{KMnO}_4$ , and 2 to 3 drops of  $\text{H}_2\text{SO}_3$ , and boil to expel brown fumes. Remove from the source of heat, cool somewhat, add about 0.5 g. of  $\text{NaBiO}_3$  (or an amount sufficient to effect either a pink color or a precipitate of  $\text{MnO}_2$ ), and boil for 2 to 3 min. Clear the solution of permanganic acid or  $\text{MnO}_2$  by the addition of a few drops of  $\text{H}_2\text{SO}_3$ , and boil to expel brown fumes. Cool to 15°C. or lower, add 0.5 g. of  $\text{NaBiO}_3$ , and complete the standardization in accordance with Sections (a) and (e) of the Procedure.

(g) **Zinc Oxide Suspension.**—Shake 50 g. of finely powdered  $\text{ZnO}$  vigorously with 300 ml. of water.

**Procedure.** 1. **Carbon Steels.**—(a) Dissolve 1 g. of the sample in 50 ml. of  $\text{HNO}_3$  (1:3) and boil until brown fumes have been expelled. Remove from the heat, cool somewhat, add about 0.5 g. of  $\text{NaBiO}_3$ , and boil for 2 to 3 min. With high-carbon steels, about 1 g. of  $\text{NaBiO}_3$ , or an amount sufficient to effect either a pink color or a precipitate of  $\text{MnO}_2$ , shall be added. Clear the solution of permanganic acid or  $\text{MnO}_2$  by adding a few drops of  $\text{H}_2\text{SO}_3$ , and boil until brown fumes have been expelled. Cool to 15°C. or lower, add 0.5 g. of  $\text{NaBiO}_3$  (or an amount equal to approximately 26 times the weight of manganese present, but not less than 0.5 g.), and agitate for 1 min. Add 50 ml. of  $\text{HNO}_3$  (3:97) and filter through a Gooch crucible or a fritted-glass or alundum filtering funnel of the Büchner type. Wash with  $\text{HNO}_3$  (3:97) until the washings run through colorless. The filtrate must be clear and absolutely free of particles of bismuthate. Complete the determination in accordance with (b) to (d), or (e) and (f) below.

**Ferrous Sulfate-Permanganate Titration.**—(b) Add 2 ml. of  $\text{H}_3\text{PO}_4$  to the filtrate. Add enough ferrous ammonium sulfate solution from a buret to discharge com-

<sup>26</sup> National Bureau of Standards' standard sample No. 55 of ingot iron is satisfactory for this purpose.

pletely the color of the permanganic acid, and then add 1 to 2 ml. in excess. Titrate with 0.03 *N*  $\text{KMnO}_4$  to the appearance of a faint pink color.

(c) **Blank.**—Make a blank determination, following the same procedure and using the same amounts of acid and bismuthate as were used with the sample. Finally, add the exact volume of ferrous ammonium sulfate solution that was used for the sample and titrate with 0.03 *N*  $\text{KMnO}_4$ .

(d) **Calculation.**—Calculate the percentage of manganese as follows:

$$\text{Manganese, per cent} = \frac{(A - B)C \times 0.0110}{D} \times 100$$

where *A* = milliliters of  $\text{KMnO}_4$  solution required to titrate the blank,  
*B* = milliliters of  $\text{KMnO}_4$  solution required to titrate the sample,  
*C* = normality of the  $\text{KMnO}_4$  solution, and  
*D* = grams of sample used

(e) **Arsenite Titration.**—After filtering off the bismuthate (Paragraph (a)), immediately titrate with sodium arsenite (1 ml. = 0.0007 g. Mn) to a clear greenish yellow color that does not change upon addition of another drop of arsenite.

(f) **Calculation.**—Calculate the percentage of manganese as follows:

$$\text{Manganese, per cent} = \frac{EF}{D} \times 100$$

where *E* = milliliters of sodium arsenite solution required to titrate the sample,  
*F* = manganese equivalent of the sodium arsenite solution, in grams per milliliter, and  
*D* = grams of sample used.

**2. Alloy Steels.**—With steels containing nickel, molybdenum, and less than 1% of chromium, determine manganese as described in Section 1 above, although it is preferable in the most accurate work to remove chromium if it is present as an essential constituent of the steel (over 0.50% chromium). This may be done by the bicarbonate separation described in Section 3(a).

**3. Chromium-Vanadium, Stainless, and Similar Steels.** (a) **Bicarbonate Separation.**—Transfer 1 g. of the sample to a 300-ml. Erlenmeyer flask, add 20 ml. of  $\text{H}_2\text{SO}_4$  (1:9), cover, and heat gently. When action is complete, dilute to 100 ml. with boiling water. Add  $\text{NaHCO}_3$  (80 g. per liter) from a buret until a permanent precipitate is formed (approximately 36 ml.) and then 4 ml. more. For high-chromium (18%) steel use a 12- to 15-ml. excess. Cover the flask, boil for 1 min., and let the precipitate settle. Filter rapidly, conveniently through a cone and paper containing a little paper pulp, wash the flask, and precipitate four or five times with hot water.<sup>27</sup> If the precipitation has been properly performed, there will be no more precipitate than can be conveniently handled on an 11-cm. paper. The filtrate will become cloudy in the funnel stem and in the receiving vessel, owing to oxidation and hydrolysis. Heat the filtrate to boiling and oxidize with

<sup>27</sup> The bicarbonate precipitate does not ordinarily contain more than small amounts (about 0.01%) of manganese. In very accurate work this should be recovered by transferring the precipitate to a beaker, dissolving it in aqua regia, fuming with  $\text{H}_2\text{SO}_4$ , and then carefully adding  $\text{Na}_2\text{O}_2$  in excess and boiling. Chromium and vanadium are thus separated from manganese and iron, which should be filtered off, dissolved in 5 ml. of  $\text{HNO}_3$  (1:1), and added to the filtrate from the bicarbonate precipitation. A drop of  $\text{H}_2\text{SO}_4$  added to the  $\text{HNO}_3$  aids in the solution of the  $\text{MnO}_2$ .

small portions of  $\text{HNO}_3$ , adding a total of 12 ml. Evaporate to about 50 ml. Add about 0.5 g. of  $\text{NaBiO}_3$  and boil 2 to 3 min. Clear the solution by adding a few drops of  $\text{H}_2\text{SO}_4$ , boil, and complete the determination as described in Section 1 above.

(b) **Zinc Oxide Separation.**—Alternatively, the zinc oxide separation of chromium and manganese may be used in place of the bicarbonate separation. Transfer 1 g. of the sample to a 400-ml. beaker, add 25 ml. of  $\text{HNO}_3$  (1:3), and heat gently. If the alloy is not attacked by  $\text{HNO}_3$ , dissolve in 25 ml. of  $\text{H}_2\text{SO}_4$  (1:5) and oxidize with 2 to 5 ml. of  $\text{HNO}_3$ . When the sample is dissolved, dilute to 200 ml., nearly neutralize with  $\text{NH}_4\text{OH}$ , and then add 5-ml. portions of the  $\text{ZnO}$  suspension until the iron is precipitated and a slight excess of  $\text{ZnO}$  is present. Shake thoroughly after each addition of  $\text{ZnO}$ . When sufficient  $\text{ZnO}$  has been added, further addition of the reagent causes the brown precipitate to appear lighter in color. A sufficient excess of  $\text{ZnO}$  is also indicated by a slightly white and milky supernatant liquid. Allow the precipitate to settle, filter through a rapid filter paper, and wash well with cold water. The  $\text{ZnO}$  precipitate will retain small amounts of manganese (about 0.01%). Add 12 ml. of  $\text{HNO}_3$  to the filtrate and evaporate to about 50 ml. Add about 0.5 g. of  $\text{NaBiO}_3$ , and boil 2 to 3 min. Clear the solution by adding a suitable reducing agent, boil, and complete the determination as described in Section 1.

4. **Cast Iron and High-Silicon Steels.**—Transfer 1 g. of the sample to a 125- or 150-ml. Erlenmeyer flask, add 25 ml. of  $\text{HNO}_3$  (1:3), heat, and boil 2 to 3 min. after action ceases. Cool, filter, and wash the flask and paper with 25 ml. of  $\text{HNO}_3$  (1:3). Wash the paper a few more times with hot water, and then complete the determination as described in Section 1, including the preliminary oxidation and boiling with  $\text{NaBiO}_3$ .

5. **Open-Hearth Iron and Wrought Iron.**—Determine manganese in accordance with the procedure described in Section 1, using 2 to 3 g. of the sample and dissolving in 100 ml. of  $\text{HNO}_3$  (1:3). It is advisable, before filtering the solution through a Gooch crucible (Section 1 (a)), to treat the asbestos pad with a weak solution of  $\text{KMnO}_4$  and then to wash it free of  $\text{KMnO}_4$  with  $\text{HNO}_3$  (3:97). Very low-manganese irons shall not be filtered through pads used previously for higher-manganese alloys.

## THE PERSULFATE METHOD (PRESENCE OF COBALT)

**Apparatus: Potentiometric Titration.**<sup>28</sup>—The essential parts of a potentiometer are shown in Fig. 24-4. The battery, *B*, produces a potential drop across the resistance wire, *R*, which will be uniform along the length, because the wire is of uniform resistance. To determine the actual magnitude of this potential drop, connect a standard cell between the terminals of the electrodes  $E_1$  and  $E_2$  in such a way as to furnish a back e.m.f. Adjust the slide *S* until the galvanometer shows no current flowing. The potential drop between *a* and *S*, produced by *B*, will then be equal to that of the standard cell. Measure the length *aS* and the total length of the wire and calculate the total potential drop by proportion.

<sup>28</sup> For further information, see the following references: Kolthoff, I. M., and Laitinen, H. A., *pH and Electro Titrations*, 2nd Ed., John Wiley and Sons, Inc., New York, 1941; Kolthoff, I. M., and Furman, N. H., *Potentiometric Titrations*, 2nd Ed., John Wiley and Sons, Inc., New York, 1931; Muller, R. H., *Instrumental Methods of Chemical Analysis*, Ind. Eng. Chem., Anal. Ed., 13, 722-727, 1941; Furman, N. H., *Potentiometric Titrations—A Review with Bibliography*, Ind. Eng. Chem., Anal. Ed., 14, 367-382, 1942; Reilly, C. N., *Potentiometric Titrations*, Anal. Chem., 28, 671-678, 1956.

In actual practice it is convenient to have a permanent calibration of the resistance scale in terms of millivolts. Changes in potential of the battery *B*, which would otherwise alter this calibration, are compensated for by variation of the

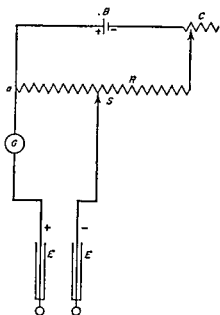


FIG. 24-4. Diagram of the Essential Parts of a Potentiometer: *B*, voltaic source; *R*, uniform resistance wire; *S*, slide contact; *G*, galvanometer; *E*, electrodes; *C*, calibration adjustment.

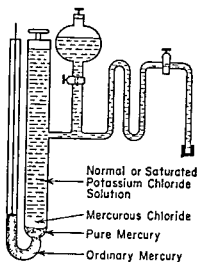


FIG. 24-5. Mercurous Chloride (Calomel) Half Cell for Potentiometric Titration.

calibration adjustment *C*. By changing the resistance at *C*, the total potential drop across *R* can be altered, within limits, to the pre-established value.

There are available commercially many fine potentiometric instruments that are accurate and convenient to operate. Most of these have sensitive vacuum tube amplifying circuits, contain a standardizing cell, and are calibrated to read potentials directly. The most common indicator electrode for oxidation-reduction measurements is bright platinum. The reference electrode most commonly used is the saturated calomel electrode. This calomel electrode may be either the commercial, pencil-type unit that is immersed directly in the solution, or may be an external cell contacting the solution by means of an agar-agar salt bridge or a salt solution bridge. An example of the latter is shown in Fig. 24-5. Many other types of electrodes and electrode pairs may be employed, the platinum-tungsten system for example.

To measure the potential of a solution, electrodes *E*<sup>+</sup> and *E*<sup>-</sup> of suitable nature are immersed in the solution. The slide *S* is adjusted to the null point as indicated by the galvanometer, and the potential is read or is calculated from the measured length *aS*, the total length of the wire, and the previously determined total potential drop along the wire.

To conduct a potentiometric titration the electrodes are immersed in the solution and the potential measured as described. A measured volume of titrant is

added from the buret, the solution is stirred, and the potential measured. Another measured volume of titrant is added, the solution is stirred, and the potential measured. This process is repeated until the reaction has been carried slightly beyond completion. It is characteristic of an oxidation-reduction titration that the greatest rate of change of potential occurs at equivalence point. This point can be readily identified by examining or plotting the data; it corresponds to the end point. In many cases it is necessary only to add titrant dropwise as the end point is approached and stop the titration when one drop is observed to produce a large change of potential.

**Reagents.** (a) **Mixed Acids.**—Add 100 ml. of  $\text{H}_2\text{SO}_4$  to 525 ml. of water slowly, while stirring. Cool, and add 125 ml. of  $\text{H}_3\text{PO}_4$  and 250 ml. of  $\text{HNO}_3$ .

(b) **Silver Nitrate Solution** (8 g. per liter).

(c) **Ammonium Persulfate Solution** (250 g. per liter).—The solution must not be kept longer than 12 hr. If the salt is of less than 95% strength, the necessary equivalent must be used.

(d) **Standard Sodium Arsenite Solution** (1 ml. = 0.0007 g. Mn).—The titration of permanganic acid with sodium arsenite by either the visual or potentiometric method is empirical. It is, therefore, necessary to standardize the arsenite solution against a like weight of a standard steel that has approximately the same manganese and chromium content as the sample being analyzed, and has been treated in exactly the same manner, except for open-hearth iron and wrought iron. For open-hearth iron and wrought iron, standardize as follows: Dissolve 1 g. of electrolytic or open-hearth iron of a known, low manganese content in 30 ml. of the mixed acids. Heat until solution is complete, and boil to expel brown fumes. Dilute to 100 ml. with hot water, add exactly 20 ml. of 0.03 *N*  $\text{KMnO}_4$ , and then add just enough  $\text{H}_2\text{SO}_3$  to reduce the  $\text{KMnO}_4$ . Boil again to expel brown fumes. Add 10 ml. of  $\text{AgNO}_3$  (8 g. per liter) and 10 ml. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (250 g. per liter). Heat to boiling and boil briskly for 60 to 90 sec. Complete the standardization in accordance with the procedure described in Section 1 (b) and (c) or (b) and (d).

**Procedure. 1. Carbon Steels.**—(a) Transfer 1 g. of the sample for a steel containing 1% or less of manganese, or 0.5 g. of the sample for a steel of higher manganese content, to a 500-ml. Erlenmeyer flask, and add 30 ml. of the mixed acids. Heat until solution is complete, and boil until brown fumes have been expelled. Add 100 ml. of hot water, 10 ml. of  $\text{AgNO}_3$  (8 g. per liter), and 10 ml. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (250 g. per liter). Heat to boiling and boil briskly for 60 to 90 sec.

(b) Add 75 ml. of water to the solution, cool to 30°C. or lower, and titrate as described in Paragraph (c) or (d).

(c) **Visual Titration.**—Titrate rapidly with sodium arsenite (1 ml. = 0.0007 g. Mn) to a clear yellow end point that does not change upon the addition of more arsenite. If the solution is not titrated rapidly with arsenite, part of the manganese may be reoxidized by the  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  during the titration and thus yield high results.

(d) **Potentiometric Titration.**<sup>29</sup>—Cool the solution to 15°C. and titrate rapidly with sodium arsenite (1 ml. = 0.00007 g. Mn). To titrate, bring the needle (or

<sup>29</sup> While the potentiometric titration offers no particular advantage over the visual method for steels containing less than 1% of manganese, it is claimed that more reproducible end points can be obtained potentiometrically with steels of high manganese content. The apparatus consists essentially of three parts, a motor stirrer, electrodes, and a



light-beam) on the scale, and then add the sodium arsenite solution. As the end point is approached (rapid fading of the pink color) the indicator will remain stationary, or move very slowly. Continue the addition of the arsenite drop by drop until a sharp break of 4 to 5 scale divisions is obtained.

(e) Calculation.—Calculate the percentage of manganese as follows:

$$\text{Manganese, per cent} = \frac{AB}{C} \times 100$$

where  $A$  = milliliters of sodium arsenite solution required to titrate the sample,  
 $B$  = manganese equivalent of the sodium arsenite solution, in grams per milliliter,  
 and  
 $C$  = grams of sample used.

**2. Nickel, Chromium-Nickel, Chromium-Vanadium, and Chromium-Vanadium-Molybdenum Steels.**—Determine manganese in accordance with the procedure described in Section 1.

**3. Chromium Steels Containing Over 4% Chromium.**—Separate the greater part of the chromium by the bicarbonate separation described in Section 3 (a) above, using a 6-ml. excess of  $\text{NaHCO}_3$  (80 g. per liter) for high-chromium (18%) steels. Add 30 ml. of the mixed acids to the filtrate, evaporate to 125 ml., and complete the determination as described in Section 1. With high-carbon (0.8%), high-chromium, chromium-molybdenum steel, test the bicarbonate precipitate for manganese.

**4. Chromium-Tungsten Steels.**—(a) To 0.5 g. of the sample, add 50 ml. of  $\text{H}_2\text{SO}_4$  (1:9) and 3 ml. of  $\text{H}_3\text{PO}_4$ . Heat until all action ceases. Add 40 ml. of water and 5 ml. of  $\text{HNO}_3$ ; boil until the carbides have dissolved, and complete the determination as described in Section 1.

(b) With chromium-tungsten steels, the arsenite solution is preferably standardized on a steel of similar type of known manganese content. Tungsten steels with high carbon (0.8%) and high-chromium (4.0%) contents may not be completely decomposed by the  $\text{H}_2\text{SO}_4$ - $\text{H}_3\text{PO}_4$  attack. In this case, dissolve the sample with 10 ml. of a mixture of equal parts of  $\text{HCl}$  and  $\text{HNO}_3$  and 4 to 5 drops of  $\text{HF}$ . When action ceases, add 4 ml. of  $\text{HClO}_4$  and evaporate just to dryness. Cool, add 5 ml. of  $\text{H}_2\text{SO}_4$ , and fume until  $\text{HClO}_4$  is expelled. Cool, add 50 ml. of water and 5 ml. of  $\text{H}_3\text{PO}_4$ , dilute to 100 ml., and heat until salts dissolve. If  $\text{MnO}_2$  appears, dissolve it with a few drops of  $\text{H}_2\text{SO}_3$ . Complete the determination as described in Section 1.

**5. Cast Iron and High-Silicon Steels.**—Add 30 ml. of water and 30 ml. of the mixed acids to the sample and dissolve as directed in Section 1 (a). Dilute to 75 ml., filter through a rapid paper, wash with hot water, dilute to 125 ml., and complete the determination as described in Section 1.

potentiometric unit. In the Larrabee apparatus the electrodes consist of gold and platinum rods with small vanes at the bottom. In the Kelley apparatus platinum and calomel electrodes are used; it is desirable to insert a salt bridge ( $\text{Na}_2\text{SO}_4$ ) solution between the calomel electrode and the titrating solution in this apparatus.

## THE PERIODATE (PHOTOMETRIC) METHOD (E30-60T) (FOR ALLOYS CONTAINING NOT MORE THAN 5% MANGANESE)

**Principle of Method.**—Manganous ions in the sample solution are oxidized to permanganate ions by treatment with periodate.

**Concentration Range.**—The recommended concentration range is from 0.2 to 0.8 mg. of manganese in 50 ml. of solution, using a cell depth of 1 cm. (Note 1) and a spectrophotometer with a band width of 10 m $\mu$  or less.

NOTE 1.—This procedure has been written for cells having a 1-cm. light path and a "narrow-band" instrument. The concentration range depends upon band width and spectral region used as well as cell depth; calibration data should cover the range of 20 to at least 70% transmittance.

**Stability of Color.**—The color is stable for at least 24 hr.

**Interfering Elements.**—The elements ordinarily present in steel do not interfere. Perchloric acid treatment, which is recommended in the procedure, yields solutions which are highly colored due to the presence of chromate ions. Although these ions and other colored ions in the sample solution undergo no further change in spectral quality upon treatment with periodate, the following precautions must be observed when filter photometers are used: select a filter with maximum transmittance between 545 and 565 m $\mu$ ; the filter must transmit not more than 5% of its maximum at a wavelength shorter than 530 m $\mu$ ; the bandwidth of the filter should be less than 30 m $\mu$  when measured at 50% of its maximum transmittance. Similar restrictions apply with respect to the wavelength region employed when other "wide-band" instruments are used.

The spectral transmittance curve of permanganate ions exhibits two useful minima, one at approximately 526 m $\mu$ , and the other at 545 m $\mu$  (Note 2). The latter is recommended when a "narrow-band" spectrophotometer is used.

NOTE 2.—Determine the exact location of the minimum for each spectrophotometer by obtaining spectral transmittance data in this spectral region and thus compensate for characteristics that are related to the instrument.

**Apparatus.** **Volumetric Flasks.**—These should be of borosilicate glass, glass-stoppered, 50- and 100-ml. capacity.

**Reagents.** (a) **Standard Manganese Solution** (1 ml. = 0.032 mg. Mn).—Dissolve 0.4000 g. of high-purity manganese (containing not less than 99.7% Mn) in 20 ml. of HNO<sub>3</sub> by heating, cool, and dilute to 500 ml. in a volumetric flask. Transfer 20 ml. of this solution to a 500-ml. volumetric flask, dilute to the mark, and mix.

(b) **Potassium Periodate Solution.**—Dissolve 7.5 g. of KIO<sub>4</sub> in 200 ml. of hot HNO<sub>3</sub> (1:1), add 400 ml. of H<sub>3</sub>PO<sub>4</sub>, cool, and dilute to 1 liter.

(c) **Nitric-Phosphoric Acid Mixture.**—To 400 ml. of water, add 100 ml. of HNO<sub>3</sub> and 400 ml. of H<sub>3</sub>PO<sub>4</sub>, and dilute to 1 liter.

(d) **Sodium Nitrite Solution** (20 g. per liter).—Dissolve 2 g. of NaNO<sub>2</sub> in water and dilute to 100 ml. (This solution is sufficiently stable for use over a 24-hr. period.)

**Preparation of Calibration Curve.** (a) **Calibration Solutions.**—By means of pipets, transfer 5, 10, 15, 20, and 25 ml. of manganese solution (1 ml. = 0.032 mg. Mn) to 50-ml. volumetric flasks, dilute to 25 ml., if necessary, and add 10 ml. of KIO<sub>4</sub> solution. (Prepare a duplicate or triplicate at each level of manganese.)

(b) **Reference Solution.**—Prepare a reference solution in a 50-ml. volumetric flask by adding 10 ml. of HNO<sub>3</sub>-H<sub>3</sub>PO<sub>4</sub> mixture to 25 ml. of water.

(c) **Color Development.**—Heat the solutions at not less than 90°C. for 20 to 30 min. Cool, dilute to volume, and mix.

(d) **Photometry.**—Fill the two 1-cm. cells with the reference solution and measure the transmittance at 545  $m\mu$ ; convert to absorbance, and record as the cell correction. Empty the test cell, rinse thoroughly with the test solution, and measure the transmittance, or the absorbance, of each test solution.

(e) **Calibration Curve.**—Apply the cell correction to each absorbance value, and calculate the average absorbance value at each level of manganese. Calculate the ratio of milligrams of manganese to absorbance at each level of manganese. If the ratios are constant within experimental error, calculate the average value of the ratios to find the factor to apply to convert absorbance to milligrams of manganese. If the ratios are not constant (Note 3), or if for other reasons it is desirable, plot the values obtained against milligrams of manganese per 50 ml. of solution.

NOTE 3.—The ratios may not be constant when "wide-band" instruments are used. Extreme deviation from linearity may indicate the need for additional values. These may be obtained by appropriate dilution of the standard manganese solution before taking additional aliquots.

**Procedure. 1. Manganese Steels Containing Less Than 0.5% Tungsten.** (a) **Sample Solution.**—Transfer the sample (Note 4), not exceeding 0.80 g., to a 100-ml. volumetric flask (Note 5). Add 8 to 10 ml. of HCl (1:1) and heat until the sample is decomposed. Add 3 to 4 ml. of  $\text{HNO}_3$  and 10 ml. of  $\text{HClO}_4$ . Fume to oxidize chromium and to expel HCl. Cool, add 50 ml. of water, and, if necessary, digest to dissolve the salts. Cool, dilute to volume, and mix. Allow insoluble matter to settle, or dry-filter before taking aliquots (Note 5).

NOTE 4.—The following sample size guide is based on the factor, ratio of milligrams of manganese to absorbance:

Mn, per cent	Sample, g. per 100 ml. <sup>a</sup>	Aliquot, ml.
0.1 to 0.5 . . . . .	0.7F	20
0.45 to 1.0 . . . . .	0.35F	20
0.85 to 2.0 . . . . .	0.17F	20
2.0 to 5.0 . . . . .	0.17F	10

<sup>a</sup> Round to two significant figures.

NOTE 5.—If the sample contains much silicon, a deposit of silicic acid will cling to the walls of the flask. Hence, it may be desirable to dissolve the samples and fume with  $\text{HClO}_4$  in an Erlenmeyer flask, and then transfer the solution to the volumetric flask. However, the deposit of silicic acid can be removed easily by means of  $\text{NH}_4\text{OH}$ .

(b) **Reference Solution.**—Transfer identical aliquots (Note 6) to each of two 50-ml. volumetric flasks; prepare one as a reference solution by adding 10 ml. of  $\text{HNO}_3$ - $\text{H}_3\text{PO}_4$  mixture.

NOTE 6.—The following procedure may be used for the preparation of the reference solution in the analysis of steels that do not contain tungsten: after filling the cell with the test solution, add  $\text{NaNO}_2$  solution dropwise to the solution remaining in the volumetric flask, while mixing the solution thoroughly, until one drop in excess has been provided

over that required to reduce the  $\text{HMnO}_4$ ; stopper the flask and mix thoroughly; fill the reference cell and measure the transmittance. (Transmittance measurement should not be postponed unduly, due to the fact that reoxidation of manganese occurs on standing.)

(c) **Test Solution.**—To the other aliquot (Paragraph (b)) add 10 ml. of  $\text{KIO}_4$  solution.

(d) **Photometry.**—Proceed with development of color and photometry in the same manner as for the preparation of the calibration curve. (If percentage transmittance is less than 20, rerun using a smaller sample.)

(e) **Calculation.**—Apply the cell correction and calculate the percentage of manganese as follows (Note 7):

$$\text{Manganese, per cent} = \frac{AFV_1}{V_2W \times 10}$$

where  $A$  = corrected absorbance,

$F$  = factor, ratio of milligrams of manganese to absorbance,

$V_1$  = dilution of sample solution in milliliters,

$V_2$  = aliquot of sample solution in milliliters, and

$W$  = grams of sample used.

NOTE 7.—If a calibration curve is used, read the value for milligrams of manganese corresponding to the absorbance from the curve. Substitute this value for  $AF$  in the equation.

2. **Tungsten Steels.** (a) **Sample Solution.**—Transfer the sample (Note 4), not exceeding 0.80 g., to a 100-ml. volumetric flask (Note 5). Add 8 to 10 ml. of  $\text{H}_3\text{PO}_4$ , 10 ml. of  $\text{HClO}_4$ , 5 to 6 ml. of  $\text{H}_2\text{SO}_4$  (1:1), and 3 to 4 ml. of  $\text{HNO}_3$ . Heat moderately until the sample is decomposed, then heat to copious white fumes and continue for 10 to 12 min. (Note 8), or until the chromium is oxidized. Cool, add 50 ml. of water, and digest, if necessary, to dissolve the salts. Cool, dilute to volume, and mix. Allow insoluble matter to settle, or dry-filter before taking aliquots (Note 5).

NOTE 8.—Excessive heating should be avoided because it will expel the  $\text{HClO}_4$  before complete oxidation of the chromium has been accomplished.

(b) Proceed according to Section 1 (b), (c), (d), and (e).

## PHOSPHORUS

### THE MOLYBDATE-MAGNESIA METHOD

**Reagents.** (a) **Potassium Permanganate Solution** (25 g. per liter).

(b) **Ammonium Molybdate Solution (Ammoniacal).**—Transfer to an 800-ml. beaker 65 g. of ammonium heptamolybdate  $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O})$ , 225 g. of  $\text{NH}_4\text{NO}_3$ , 15 ml. of  $\text{NH}_4\text{OH}$ , and 600 ml. of water. Stir and heat gently. When the crystals have dissolved, filter (without washing), and dilute to 1 liter with water.

(c) **Magnesia Mixture.**—Dissolve 130 g. of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and 75 g. of  $(\text{NH}_4)_2\text{SO}_4$  in 500 ml. of water. Add  $\text{NH}_4\text{OH}$  in slight excess and let stand overnight. Filter if a precipitate appears. Make just acid by adding a very slight excess of  $\text{H}_2\text{SO}_4$ , dilute to 1 liter, and keep in a glass-stoppered bottle.

(d) **Ammonium Nitrate Wash Solution.**—Dissolve 50 g. of  $\text{NH}_4\text{NO}_3$  in 1 liter of  $\text{NH}_4\text{OH}$  (1:20).

(e) **Ferrous Sulfate Solution.**—Dissolve 100 g. of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 1 liter of  $\text{H}_2\text{SO}_4$  (5:95).

**Procedure. 1. Carbon Steels.**—(a) Transfer 3 g. of the sample<sup>30</sup> to a 300 ml Erlenmeyer flask, dissolve the sample in 125 ml. of  $\text{HNO}_3$  (1:3), oxidize the organic matter by adding 10 ml. of  $\text{KMnO}_4$  (25 g. per liter), and boil for 3 to 5 min. If no precipitate forms, add more  $\text{KMnO}_4$  and boil again. Dissolve the precipitate by the addition of  $\text{H}_2\text{SO}_4$  drop by drop, and boil for a few minutes to expel oxides of nitrogen. Cool to about  $75^\circ\text{C}$ ., and add 85 ml. of ammoniacal ammonium molybdate solution. Stopper the flask, shake for 10 min., and allow to stand for 2 hr. or more. Filter through a close-texture paper. Wash the flask, precipitate, and paper six to eight times with cold  $\text{HNO}_3$  (2:98).

(b) Set the filtrate and washings aside after thorough mixing, and note whether further separation of phosphomolybdate occurs. Dissolve the precipitate on the filter and in the flask in a mixture of 20 ml. of  $\text{NH}_4\text{OH}$  (1:1) and 2 g. of citric acid, catching the solution in a 250-ml. beaker. Wash the filter several times with  $\text{NH}_4\text{OH}$  (1:20), then with hot water, and finally several times with  $\text{HCl}$  (1:20). If the ammoniacal solution of the phosphomolybdate is not clear at this point, heat it to boiling and filter through the same paper. Wash the paper with hot water, ignite in a small platinum crucible, and fuse any residue with as little  $\text{Na}_2\text{CO}_3$  as possible (not over 0.5 g.). Extract the cooled melt with hot water, cool, filter, and add the water solution to the ammoniacal solution.

(c) Acidify the combined solutions with  $\text{HCl}$ , add 20 ml. of magnesia mixture, cool in ice water, and then add  $\text{NH}_4\text{OH}$  slowly until the solution is just ammoniacal. Stir vigorously for 5 min. or until a crystalline precipitate appears,<sup>31</sup> and add 5 to 10 ml. of  $\text{NH}_4\text{OH}$ . The volume of the solution at this point should not exceed 100 ml. Allow the solution to stand in a cool place for 4 to 6 hr. or, preferably, overnight. Filter and wash the precipitate moderately with  $\text{NH}_4\text{OH}$  (1:20).

(d) Dissolve the precipitate on the filter in 20 ml. of  $\text{HCl}$  (1:1), catching the solution in the original beaker. Wash the filter thoroughly with warm  $\text{HCl}$  (1:1). Add 0.5 to 1 g. of  $\text{NH}_4\text{Br}$ <sup>32</sup> and gently boil the solution to a volume of 5 to 10 ml. (but not to dryness) to eliminate arsenic. Dilute to 50 to 75 ml., add 0.1 to 0.2 g. of citric acid and 2 to 3 ml. of magnesia mixture, and cool in ice water. Make ammoniacal, stir as before, and allow to stand in a cool place for 4 to 24 hr.

(e) Filter, and wash with  $\text{NH}_4\text{NO}_3$  wash solution. Ignite the precipitate in a platinum crucible, carefully and at as low a temperature as possible, until the carbon has been destroyed and the residue is white. Finally, ignite to constant weight at 1000 to  $1050^\circ\text{C}$ .

(f) Dissolve the ignited precipitate in 5 ml. of  $\text{HNO}_3$  (1:1) and 20 ml. of water. If no residue remains, the ignited precipitate may be regarded as  $\text{Mg}_2\text{P}_2\text{O}_7$ . If a residue remains, filter, wash with hot water, ignite, and weigh. Add a few drops of  $\text{HF}$  and 1 to 2 drops of  $\text{H}_2\text{SO}_4$  (1:1). Evaporate to dryness, ignite at  $1000^\circ\text{C}$ ., and weigh again. The loss in weight represents the correction for impurities.

<sup>30</sup> If the phosphorus content is less than 0.05%, it is advantageous to treat two or more 3-g. samples as described, and combine the yellow precipitates either by filtering through the same paper or by combining the precipitates after filtering on separate papers.

<sup>31</sup> If the amount of phosphorus is very small, it may take 30 min. to 1 hr. before the precipitate begins to appear.

<sup>32</sup> With a precipitation temperature of  $25^\circ\text{C}$ ., arsenic, when present in small amounts, is not precipitated and, therefore, the treatment with  $\text{NH}_4\text{Br}$  can be omitted.

(g) **Calculation.**—Calculate the percentage of phosphorus as follows:

$$\text{Phosphorus, per cent} = \frac{(A - B) \times 0.278}{C} \times 100$$

where  $A$  = grams of  $\text{Mg}_2\text{P}_2\text{O}_7$  (Paragraph (e)),

$B$  = correction for impurities (Paragraph (f)), in grams, and

$C$  = grams of sample used.

**2. Nickel, Chromium-Nickel, Stainless, and Similar Alloy Steels Containing Neither Tungsten nor Vanadium.**—(a) Determine phosphorus in accordance with the procedure described in Section 1.

(b) High-chromium steels (stainless), high-chromium, high-nickel steels (18% chromium, 8% nickel; 20% chromium, 20% nickel), and other steels in this group that do not dissolve in  $\text{HNO}_3$  (1:3), shall be treated as follows: Transfer 3 g. of the sample to a 500-ml. Erlenmeyer flask, add 75 ml. of a mixture of equal parts of  $\text{HCl}$  and  $\text{HNO}_3$ , and heat gently. When decomposition is complete, add 20 ml. of  $\text{HClO}_4$ , and evaporate to white fumes. Continue the heating for 5 min. to oxidize chromium and to dehydrate  $\text{SiO}_2$ . Cool somewhat, add 40 ml. of water, and filter. Wash the flask, paper, and residue with 55 ml. of  $\text{HNO}_3$  (3:5). Add 10 ml. of  $\text{KMnO}_4$  (25 g. per liter) to the filtrate, boil 3 to 5 min., add  $\text{H}_2\text{SO}_3$  to destroy oxides of manganese and to reduce all of the chromium, and complete the determination as described in Section 1.

**3. Austenitic Manganese Steels (Over 10% Manganese).**—Transfer 3 g. of the sample to a 300-ml. Erlenmeyer flask, add 70 ml. of  $\text{HNO}_3$  (1:3), and digest until action ceases. Add 30 ml. of  $\text{HClO}_4$  and evaporate just to fumes. Add  $\text{HF}$  drop by drop until all of the  $\text{SiO}_2$  is in solution, and then add an excess of 5 drops. Fume so that the  $\text{HClO}_4$  refluxes on the sides of the flask for 25 to 30 min. Cool, and add 50 ml. of water and 10 ml. of  $\text{HNO}_3$ . Add a few drops of  $\text{KMnO}_4$  (25 g. per liter), and boil until oxides of manganese are precipitated. Dissolve the precipitated manganese with  $\text{H}_2\text{SO}_3$ , and boil a few minutes to expel oxides of nitrogen. Cool to about  $75^\circ\text{C}$ ., precipitate with ammonium molybdate, and complete the determination as described in Section 1.

**4. Chromium-Vanadium Steels or Other Steels Containing Vanadium but No Tungsten.**—(a) Proceed as described in Section 1 (a) until the solution is ready for the addition of the molybdate reagent. At this point, cool to  $10^\circ\text{C}$ . and add 5 ml. of  $\text{FeSO}_4$  solution and 2 to 3 drops of  $\text{H}_2\text{SO}_3$ . Mix, add 85 ml. of ammonium molybdate solution, shake for 10 min., and allow to stand for 4 hr. or, preferably, overnight.

(b) Filter and complete the determination as described in Section 1.

**5. High-Speed Steels or Other Steels Containing Tungsten and Vanadium.**—(a) Decompose 3 g. of the sample in 125 ml. of  $\text{HNO}_3$  (1:3), add 30 ml. of  $\text{HCl}$ , and evaporate to dryness. Dissolve the residue with 20 ml. of  $\text{HCl}$  (1:1), dilute to 100 ml. with hot water, and filter off the tungstic acid.<sup>33</sup>

<sup>33</sup> This precipitate may contain a small amount of phosphorus, and in standardization work, shall be treated as follows: Transfer the bulk of the precipitate to an Erlenmeyer flask with a jet of water, and then treat the paper with 25 ml. of hot  $\text{NH}_4\text{OH}$  (1:4) containing 0.5 g. of citric acid. Catch the filtrate in the flask containing the remainder of the precipitate. Wash the paper with hot water, then a few times with hot  $\text{HCl}$  (1:20), holding the volume of the filtrate and washings to about 75 ml. Slightly acidify the solution with  $\text{HCl}$ , add 25 ml. of magnesia mixture, and add about 10 ml. of  $\text{NH}_4\text{OH}$  in

(b) Evaporate the filtrate twice with 20-ml. portions of  $\text{HNO}_3$  to expel the  $\text{HCl}$ , taking the second evaporation just to a sirup. Add 65 ml. of  $\text{HNO}_3$  (1:3), and filter the solution if it is not entirely clear. Cool to  $10^\circ\text{C}$ . Add 5 ml. of  $\text{FeSO}_4$  solution and 2 to 3 drops of  $\text{H}_2\text{SO}_4$ . Mix, add 85 ml. of ammonium molybdate solution, shake for 10 min., and allow to stand for 4 hr. or, preferably, overnight.

(c) Filter and complete the determination as described in Section 1.

**6. Cast Iron and High-Silicon Steels.**—(a) Dissolve 2 to 3 g. of the sample in a covered casserole in 30 ml. of  $\text{HNO}_3$  (1:1). When solution is complete, add 10 ml. of  $\text{HCl}$  (1:1), evaporate to dryness, and bake for 15 to 20 min. on the hot plate.

(b) Cool, drench the residue with  $\text{HCl}$ , dilute to 50 ml. with hot water, and warm until the salts are in solution. Filter without delay, wash with  $\text{HCl}$  (1:20), and evaporate the filtrate to sirupy consistency.

(c) In the meantime, place the paper containing the graphite and silica in a platinum crucible, burn the carbon in a good oxidizing atmosphere, cool, and add 5 to 10 drops of  $\text{HCl}$  and 1 to 2 ml. of  $\text{HF}$ . Evaporate just to dryness, take up any residue<sup>34</sup> in 5 ml. of  $\text{HCl}$ , and add the solution to the main solution which is being evaporated.

(d) When the solution is of sirupy consistency, transfer it to a 300-ml. Erlenmeyer flask by alternate washing with  $\text{HNO}_3$  (1:1) and hot water, using about 40 ml. of  $\text{HNO}_3$  (1:1) and 70 ml. of hot water. Adjust the temperature of the solution to about  $70^\circ\text{C}$ ., and add 100 ml. of ammonium molybdate solution. Shake for 10 min. and allow to stand for 4 to 6 hr. or, preferably, overnight.

(e) Filter and complete the determination as described in Section 1.

**7. Open-Hearth Iron and Wrought Iron.**—Determine phosphorus in accordance with the procedure described in Section 1.

## THE ALKALIMETRIC METHOD

**Reagents.** (a) Potassium Permanganate Solution (25 g. per liter).

(b) Ammonium Molybdate Solution (Ammoniacal).

(c) Standard Sodium Hydroxide Solution (1 ml. = 0.0002 g. P, approximately 0.15 N).—Standardize against the National Bureau of Standards' standard sample of acid potassium phthalate, using the ratio 23 NaOH to 1 phosphorus. One milliliter of 1 N NaOH is equivalent to 0.00135 g. of phosphorus. Protect the NaOH solution from  $\text{CO}_2$  by means of a soda-lime or soda-asbestos tube.

(d) Standard Nitric Acid.—Dilute 10 ml. of clear  $\text{HNO}_3$  to 1 liter with water and standardize against the standard NaOH solution, using phenolphthalein as the indicator. If desired, the  $\text{HNO}_3$  may be rendered equivalent to the NaOH solution by dilution with water.

(e) Phenolphthalein Indicator.—Dissolve 0.2 g. of phenolphthalein in 100 ml. of ethanol (50%).

excess. Add a few glass beads, cool the solution in ice water, stopper the flask, and shake thoroughly for 1 hr. Allow to stand overnight at about  $0^\circ\text{C}$ . Filter, and wash a few times with  $\text{NH}_4\text{OH}$  (1:20). Dissolve the precipitate in a little hot  $\text{HNO}_3$  (1:3) and add it to the original solution in which phosphorus is to be determined, or determine the phosphorus separately by precipitating it with ammonium molybdate solution and titrating with standard NaOH and  $\text{HNO}_3$  (Section 1 under Alkalimetric Method below). This recovery usually amounts to less than 0.001% and need not be made in routine analyses.

<sup>34</sup> If the percentage of titanium or zirconium is high, this residue should be fused with  $\text{Na}_2\text{CO}_3$ , extracted with hot water, cooled, filtered, and the water extract added to the main solution.

(f) **Ferrous Sulfate Solution.**—Dissolve 100 g. of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 1 liter of  $\text{H}_2\text{SO}_4$  (5:95).

**Procedure. 1. Carbon Steels.**—(a) Transfer 2 g. of the sample to a 300-ml. Erlenmeyer flask. Dissolve the sample in 65 ml. of  $\text{HNO}_3$  (1:3), and oxidize organic matter by adding 10 ml. of  $\text{KMnO}_4$  (25 g. per liter) and boiling for 2 to 3 min. If no precipitate forms, add more  $\text{KMnO}_4$  and boil again.

(b) Dissolve the precipitate by adding  $\text{H}_2\text{SO}_3$  drop by drop, and boil for a few minutes to expel oxides of nitrogen. Adjust the volume to 60 ml. and the temperature to  $45^\circ\text{C}$ ., and add 50 ml. of ammonium molybdate solution. Stopper the flask, shake for 10 min., and allow the precipitate to settle for 20 min. at room temperature. Filter through a 9-cm. close-texture paper. Wash the flask, precipitate, and paper twice with 5-ml. portions of  $\text{HNO}_3$  (2:98) and then five times with 5-ml. portions of  $\text{KNO}_3$  (10 g. per liter). Finally, wash the paper about ten times (until free of acid), directing the jet of  $\text{KNO}_3$  solution around the edge of the paper and then spirally down.

(c) Return the paper and precipitate to the flask, add 25 ml. of water and a 2- to 5-ml. excess of  $\text{NaOH}$  (1 ml. = 0.0002 g. P), both free of  $\text{CO}_2$ , and shake or stir until the precipitate is dissolved. Dilute to about 150 ml. with water free of  $\text{CO}_2$ , add 3 drops of phenolphthalein indicator, and titrate with the standard  $\text{HNO}_3$  to the disappearance of the pink color.

(d) **Blank.**—Make a blank determination, following the same procedure and using the same amounts of all reagents.

(e) **Calculation.**—Calculate the percentage of phosphorus as follows:

$$\text{Phosphorus, per cent} = \frac{[(A - BC) - (D - EC)]F}{G} \times 100$$

where  $A$  = milliliters of  $\text{NaOH}$  solution required by the sample (Paragraph (c)),

$B$  = milliliters of  $\text{HNO}_3$ , required by the sample (Paragraph (c)),

$C$  = milliliters of  $\text{NaOH}$  solution equivalent to 1 ml. of the  $\text{HNO}_3$ ,

$D$  = milliliters of  $\text{NaOH}$  solution required by the blank (Paragraph (d)),

$E$  = milliliters of  $\text{HNO}_3$  required by the blank (Paragraph (d)),

$F$  = phosphorus equivalent of the  $\text{NaOH}$  solution, in grams per milliliter, and

$G$  = grams of sample used.

**2. Nickel, Chromium-Nickel, Stainless, and Similar Alloy Steels Containing Neither Tungsten nor Vanadium.**—(a) Determine phosphorus in accordance with the procedure described in Section 1.

(b) With high-chromium nickel steels or other steels insoluble in  $\text{HNO}_3$  (1:3), treat 2 g. of the sample with 50 ml. of a mixture of equal parts  $\text{HNO}_3$  and  $\text{HCl}$ , add 4 to 5 drops of  $\text{HF}$ , heat until action ceases, and then add 15 ml. of  $\text{HClO}_4$ . Evaporate to copious white fumes, fume 5 to 10 min., filter, and wash as described in Section 2 (b) of the Molybdate-Magnesia Method. Complete the determination as described in Section 1. With steels of appreciable titanium or zirconium contents (over 0.25%) the alkalimetric method tends to give low values.

**3. Austenitic Manganese Steels (Over 10% Manganese).**—(a) Transfer 2 g. of the sample to a 400-ml. beaker, add 35 ml. of  $\text{HNO}_3$  (1:3), and digest until action ceases. Add 15 ml. of  $\text{HClO}_4$  and evaporate just to white fumes. Add  $\text{HF}$  drop by drop until all of the hydrated silica is dissolved, and then add an excess of 5 drops. Heat so that  $\text{HClO}_4$  refluxes on the sides of the beaker for 20 to 25 min.



Cool and add 50 ml. of water and 10 ml. of  $\text{HNO}_3$ . Add a few drops of  $\text{KMnO}_4$  (25 g. per liter) and boil until oxides of manganese are precipitated. Dissolve the precipitated manganese with  $\text{H}_2\text{SO}_3$  and boil for a few minutes to expel oxides of nitrogen.

(b) Transfer the solution to a 300-ml. Erlenmeyer flask, adjust the volume to 60 ml. and the temperature to  $45^\circ\text{C}$ .,<sup>35</sup> and complete the determination as directed in Section 1 (b) to (e).

**4. Chromium-Vanadium Steels or Other Steels Containing Vanadium but No Tungsten.**—Proceed in accordance with Section 1 until the solution is ready for the addition of ammonium molybdate. At this point, cool to  $10^\circ\text{C}$ . and add 5 ml. of  $\text{FeSO}_4$  solution and 2 to 3 drops of  $\text{H}_2\text{SO}_3$ . Mix, and then add 50 ml. of ammonium molybdate solution. Shake for 10 min., allow to settle 1 hr., filter, and complete the determination as described in Section 1.

**5. High-Speed Steels or Other Steels Containing Tungsten and Vanadium.**—Dissolve 2 g. of the sample and prepare the solution for the precipitation of the ammonium phosphomolybdate as described in Section 5 of the Molybdate-Magnesia Method. Precipitate the phosphorus in a cool ( $10^\circ\text{C}$ .), reduced solution and complete the determination in accordance with Section 4.

**6. Cast Iron and High-Silicon Steels.**—(a) Dissolve 0.5 to 2 g. of the sample in 65 ml. of  $\text{HNO}_3$  (1:3). Filter through a loose-texture paper and catch the filtrate in a 300-ml. Erlenmeyer flask. Wash the paper a few times with  $\text{HNO}_3$  (2:98) and then with about 50 ml. of hot water.

(b) Add 10 ml. of  $\text{KMnO}_4$  (25 g. per liter) to the filtrate and boil for 3 to 5 min. Dissolve the precipitated oxides by the addition of  $\text{H}_2\text{SO}_3$  drop by drop, and boil for a few minutes to expel oxides of nitrogen. Cool to  $45^\circ\text{C}$ ., add 50 ml. of ammonium molybdate solution, and complete the determination as described in Section 1.

**7. Open-Hearth Iron.**—Determine phosphorus as directed in Section 1, dissolving 3 g. of sample in 85 ml. of  $\text{HNO}_3$  (1:3).

**8. Wrought Iron.**—Determine phosphorus in accordance with the procedure described in Section 1, but use 1 g. of the sample. In wrought iron, phosphorus will be present as phosphide and as phosphate (in slag inclusions). If a differentiation between the two forms is desired, determine total phosphorus in one sample; determine the phosphate that is left after phosphine has been driven off (by attack with a nonoxidizing acid such as  $\text{HCl}$ ) from another sample. The phosphorus occurring as phosphide is then obtained by difference. The accuracy of the results obtained by this phosphate-phosphide method is somewhat doubtful, but the method is apparently the only one available.

## THE MOLYBDENUM BLUE (PHOTOMETRIC) METHOD (E30-60T)

**Scope and Application.**—This method is recommended for cast iron, plain carbon, and alloy steels containing 0.002 to 0.30% phosphorus. The method is not recommended for tungsten steels.

**Summary of Method.**—(a) Phosphorus reacts with ammonium molybdate to form a phosphomolybdenum complex. The latter is reduced by hydrazine sulfate to

<sup>35</sup> If the solution at this point contains silica, filter, wash with water, boil until the volume of the filtrate is approximately 60 ml., and again cool to  $45^\circ\text{C}$ .

form the molybdenum blue complex which is suitable for photometric measurement.

(b) After dissolution of the sample in aqua regia, the solution is fumed with perchloric acid. The insoluble silica is removed and an aliquot is treated with sodium sulfite and ammonium molybdate-hydrazine sulfate solution to develop a colored complex. The phosphate forms the heteropolyphosphomolybdate which is reduced by the hydrazine sulfate to form the strongly colored "molybdenum blue" complex of uncertain composition. Photometric measurement is made at approximately 700  $m\mu$  or 830  $m\mu$  depending on the concentration.

**Concentration Range.**—The recommended concentration ranges, in milligrams per 100 ml., are 0.002 to 0.05 (for measurement at 830  $m\mu$ ) and 0.05 to 0.3 (for measurement at 700  $m\mu$ ) (Note 9).

NOTE 9.—This procedure has been written for a cell having a 1.0-cm. light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amount of sample and reagents used.

**Stability of Color.**—The heteropoly molybdenum blue color is stable for at least 2 hr. after development of color.

**Interferences.**—None of the elements usually present in cast iron or steel alloys interfere except arsenic, which must be removed. Tungsten also causes interference.

**Apparatus.** (a) **Glassware.**—Freedom of the glassware from phosphorus is of primary importance. Since many of the detergents commonly used contain phosphorus, the use of such detergents should be avoided on the glassware used in the following operations. Boiling with hydrochloric acid, followed by rinsing with water, is one of the best means of cleansing glassware that has become contaminated with phosphorus. As a further safeguard, it is recommended that the glassware used for this determination be reserved for this use only.

(b) **Photometers and Photometric Practice.**—Photometers and photometric practice prescribed in these methods shall conform to the Recommended Practice for Photometric Methods for Chemical Analysis of Metals (ASTM Designation: E60). A filter-type photometer will provide satisfactory accuracy for most analyses. However, a spectrophotometer may be used if desired.

**Reagents.** (a) **Ammonium Molybdate Solution** (20 g. per liter).—Add 300 ml. of  $H_2SO_4$  to 500 ml. of water and cool. Add 20 g. of ammonium heptamolybdate  $((NH_4)_6Mo_7O_{24} \cdot 4H_2O)$  and dilute to 1 liter.

(b) **Ammonium Molybdate-Hydrazine Sulfate Solution.**—Dilute 250 ml. of the ammonium molybdate solution to 600 ml., add 100 ml. of the  $(NH_2)_2 \cdot H_2SO_4$  solution, and dilute to 1 liter. Prepare immediately before use.

(c) **Aqua Regia.**—Mix 1 volume of  $HNO_3$  with 3 volumes of  $HCl$ .

(d) **Hydrazine Sulfate Solution** (1.5 g. per liter).—Dissolve 1.5 g. of hydrazine sulfate  $((NH_2)_2 \cdot H_2SO_4)$  in water and dilute to 1 liter.

(e) **Phosphorus, Standard Solution** (1 ml. = 0.05 mg. P).—Dissolve 0.2292 g. of sodium monohydrogen phosphate ( $Na_2HPO_4$ ) in about 200 ml. of water. Add 100 ml. of  $HClO_4$  (1:5) and dilute to 1 liter in a volumetric flask.

(f) **Phosphorus, Standard Solution** (1 ml. = 0.5 mg. P).—Dissolve 2.2916 g. of  $Na_2HPO_4$  in about 200 ml. of water. Add 100 ml. of  $HClO_4$  (1:5) and dilute to 1 liter in a volumetric flask.

(g) Sodium Sulfite Solution (100 g. per liter).—Dissolve 100 g. of sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) in water and dilute to 1 liter. Prepare as needed.

**Preparation of Calibration Curve.** (1) *Iron and Steel Containing 0.002 to 0.05% Phosphorus.*—(a) Transfer 1.000 g. of low-phosphorus steel (less than 0.005% P) to each of seven 100-ml. beakers. Add slowly, in small portions, 15 ml. of aqua regia. When the violent reaction has ceased, add 10 ml. of  $\text{HClO}_4$ .

(b) Carry one sample through as a blank, and to the other add 1.0, 2.0, 4.0, 6.0, 8.0, and 10.0-ml. aliquots of phosphorus solution (1 ml. = 0.05 mg. P).

(c) Evaporate the covered solutions, including the blank, to copious white fumes, fume for 15 min. and cool (Note 10).

NOTE 10.—The solution should completely solidify on cooling. If it does not, fume for another 5 min. or as long as may be necessary.

(d) After cooling, add 50 ml. of hot water to dissolve the soluble salts. Filter into a 100-ml. volumetric flask and wash the insoluble matter with hot water until about 90 ml. has been collected in the flask. Cool to  $20^\circ\text{C}$ ., dilute to the mark, and mix.

(e) Transfer a 10-ml. aliquot (Note 11) to a 100-ml. volumetric flask, add 1 ml. of  $\text{HClO}_4$  and 15 ml. of  $\text{Na}_2\text{SO}_3$  solution, boil gently for 30 sec., and immediately add 50 ml. of freshly prepared ammonium molybdate-hydrazine sulfate solution.

NOTE 11.—A 10-ml. aliquot represents, for example, 0.02 mg. of phosphorus in a sample containing 0.02% phosphorus.

(f) Heat on a steam bath at  $85$  to  $90^\circ\text{C}$ . for 20 min., and then quickly cool to  $20^\circ\text{C}$ . Dilute to the mark and mix.

(g) **Photometry.**—Transfer a portion of the reference (blank) solution to an absorption cell and adjust the photometer to the initial setting, using a light band centered at approximately  $830\text{ m}\mu$ . While maintaining this photometric adjustment, take the photometric readings of the calibration solutions.

(h) **Calibration Curve.**—Plot the photometric readings of the calibration solutions against milligrams of phosphorus per 100 ml. of solution.

(2) *Iron and Steel Containing 0.05 to 0.30% Phosphorus.*—(a) Proceed in accordance with Section (1) above.

(b) Carry one sample through as a blank, and to the others add 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0-ml. aliquots of the standard phosphorus solution (1 ml. = 0.5 mg. P).

(c) Proceed in accordance with Section (1) (c) to (f).

(d) **Photometry.**—Transfer a portion of the reference (blank) solution to an absorption cell and adjust the photometer to the initial setting, using a light band centered at approximately  $700\text{ m}\mu$ . While maintaining this photometric adjustment, take the photometric readings of the calibration solutions.

(e) **Calibration Curve.**—Plot the photometric readings of the calibration solutions against milligrams of phosphorus per 100 ml. of solution.

**Procedure.**—(a) Transfer 1.000 g. of the sample to a 100-ml. beaker.

(b) Carry through a blank on the reagents.

(c) Proceed in accordance with Section (1) (a) and (c) (Note 12).

NOTE 12.—For high-chromium steels, fuming will be sufficient when red chromic acid, condensed on the walls, reaches the top of the beaker.

(d) If arsenic is present, add 20 ml. of hydrobromic acid ( $\text{HBr}$ ) (1:4), 1 ml. of  $\text{HClO}_4$ , and evaporate again to copious white fumes to volatilize the arsenic.

(e) Proceed in accordance with Section (1) (d) to (f).

(f) **Photometry.**—Transfer a portion of the reference solution (reagent blank) to an absorption cell and adjust the photometer to the initial setting, using a light band centered at approximately 700 m $\mu$ . If the transmission reading of the sample solution is 80% or greater at the 700 m $\mu$  setting, use a light band centered at approximately 830 m $\mu$  (Note 13).

NOTE 13.—For steel containing 10% or more of chromium, the photometric measurement shall be made at 830 m $\mu$ .

**Calculation.**—Convert the photometric reading of the sample solution to milligrams of phosphorus by means of the appropriate calibration curve. Calculate the percentage of phosphorus as follows:

$$\text{Phosphorus, per cent} = \frac{A}{B \times 10}$$

where  $A$  = milligrams of phosphorus found in the aliquot used, and  
 $B$  = grams of sample represented in the aliquot used.

## SULFUR

### THE GRAVIMETRIC METHOD

**Reagents.** (a) Zinc (20- to 30-mesh, low-sulfur).

(b) Barium Chloride Solution (100 g. per liter).

(c) Copper-Potassium Chloride Solution.—Dissolve 300 g. of  $\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$  in a mixture of 1 liter of water and 75 ml. of HCl.

(d) Cinchonine Solution.—Dissolve 125 g. of cinchonine in 1 liter of HCl (1:1). If the cinchonine contains excessive quantities of sulfates, wash the crystals on a Büchner funnel with water until the washings no longer give a precipitate with  $\text{BaCl}_2$ , before dissolving in the acid.

(e) Cinchonine Wash Solution.—Dilute 30 ml. of cinchonine solution to 1 liter with water.

**Procedure. 1. Carbon Steels.**—(a) Dissolve 5 g. of the sample in 75 ml. of  $\text{HNO}_3$  <sup>36</sup> in a covered beaker or flask. In case solution is slow or difficult, HCl may be added drop by drop at intervals. With steels that dissolve too rapidly, it is necessary to place the cooled acid in a covered beaker and add the sample in small portions. When solution is complete, add 0.5 g. of  $\text{Na}_2\text{CO}_3$  and carefully evaporate <sup>37</sup> to about 10 ml. in a low-sulfur atmosphere. Cool, add 30 ml. of HCl, and evaporate just to dryness. Add 30 ml. more of HCl, and evaporate to sirupy consistency.

(b) Add 10 ml. of HCl, 25 ml. of water, and 5 g. of 20- to 30-mesh, low-sulfur zinc. Warm on a steam bath until the iron is reduced to the ferrous state and the evolution of hydrogen has nearly ceased. Filter through a close-texture paper and wash with 75 ml. of HCl (1:99).

(c) Warm the filtrate to 60 to 70°C. and add 20 ml. of  $\text{BaCl}_2$  (100 g. per liter)

<sup>36</sup> The addition of 2 to 5 ml. of bromine is claimed to effect more complete recovery of sulfur.

<sup>37</sup> The use of a coarse screen of  $\frac{1}{8}$ -in. wire, triangles, or an asbestos pad on the hot plate permits more rapid evaporation without the danger of spattering.

dropwise with constant stirring.<sup>38</sup> Let stand for 2 hr. on a steam bath and then overnight at room temperature. Filter on a 9-cm. close-texture paper and discard the filtrate. Wash once or twice with cold HCl (1:500) and then with hot water until free of chlorides. Reserve the precipitate.

(d) Add 2 ml. of  $\text{BaCl}_2$  (100 g. per liter) to the washings and evaporate just to dryness. To the residue add 2 ml. of HCl (1:1) and 25 ml. of warm water, and digest at 60 to 70°C. for several hours. Filter on a small close-texture paper and wash with hot water until free of chlorides.<sup>39</sup>

(e) Ignite both papers (Paragraphs (c) and (d)) in a weighed platinum crucible. Add 1 drop of  $\text{H}_2\text{SO}_4$  (1:1) and 1 ml. of HF. Evaporate to dryness, ignite, and weigh as  $\text{BaSO}_4$ .

(f) Blank.—Make a blank determination, following the same procedure and using the same amounts of all reagents.

(g) Calculation.—Calculate the percentage of sulfur as follows:

$$\text{Sulfur, per cent} = \frac{(A - B) \times 0.1374}{C} \times 100$$

where  $A$  = grams of  $\text{BaSO}_4$ ,

$B$  = correction for blank, in grams, and

$C$  = grams of sample used.

**2. Alloy Steels.**—(a) For steels that can be dissolved in  $\text{HNO}_3$  or in  $\text{HNO}_3$  plus small portions of HCl, determine sulfur in accordance with the procedure described in Section 1. Dissolve high-chromium-nickel steels in a 400-ml. tall form beaker in 125 ml. of a mixture of equal parts of  $\text{HNO}_3$  and HCl. First, mix the acids thoroughly in another container. When the mixture is thoroughly red, add it to the beaker containing the sample. If the reaction proceeds too rapidly, the beaker and contents should be chilled by placing them in ice water. Complete the determination as described in Section 1.

(b) **Meineke Method.**—Alternatively, the Meineke method (solution in acid copper-potassium chloride) may be used for the chromium-nickel alloys. Dissolve 5 g. of the sample in 250 ml. of copper-potassium chloride solution at room temperature and with slow mechanical stirring.<sup>40</sup> Filter through a Gooch crucible having a removable bottom, and wash two or three times with HCl (2:98). Return the residue and asbestos pad to the beaker and add 20 ml. of  $\text{HNO}_3$ . Heat and add  $\text{KClO}_3$  until all carbonaceous matter is destroyed. Graphite may be ignored. Evaporate the solution to dryness, add 10 ml. of HCl, and again evaporate to dryness. Take up in 10 ml. of HCl (1:9) and 20 ml. of water, filter through paper, and wash with 50 ml. of hot water. Heat the filtrate to boiling and add 5 ml. of  $\text{BaCl}_2$  (100 g. per liter) dropwise with constant stirring. Let stand for 2 hr. on a steam bath and then overnight at room temperature. Filter and complete the determination as described in Section 1 (c) to (g).

**3. Tungsten Steels.**—(a) Transfer 5 g. of the sample to a 600-ml. beaker or Erlenmeyer flask and add 75 ml. of  $\text{HNO}_3$ . If reaction is slow, heat gently; if it is vigor-

<sup>38</sup> The solution should preferably contain not more than 2% by volume of HCl at the time of the precipitation with  $\text{BaCl}_2$ . Ordinarily, there will be no hydrolysis of iron during the filtration and washing of the undissolved zinc or the precipitation with  $\text{BaCl}_2$ . Should this occur, the solution must be cleared by the addition of HCl, having due regard to the final permissible acidity.

<sup>39</sup> This recovery of  $\text{BaSO}_4$  ordinarily represents from 0.001 to 0.003% of sulfur.

<sup>40</sup> Selenium is also obtained with sulfur in the residue; hence, with selenium steels, all operations should be conducted under a good hood.

ous, cool in ice water. If reaction is very slow, add 5 ml. of HCl or a drop or two of HF occasionally while heating the solution on a steam bath. When  $\text{HNO}_3$  alone is used, the particles of steel tend to become covered with a film of tungstic acid. Stirring or rubbing these coated granules speeds up the decomposition. When reaction is complete, digest until the residue is pure yellow and contains no dark material, adding fresh portions of acid if necessary. Evaporate to sirupy consistency. Cool, add 30 ml. of HCl, and again evaporate to sirupy consistency. Add 100 ml. of hot water and boil until soluble salts are in solution. Filter and wash the residue with HCl (1:10), catching the filtrate and washings in a 600-ml. casserole.

(b) Evaporate to dryness, add 30 ml. of HCl, and again evaporate to dryness. Cool, add 60 ml. of HCl (1:1), warm until salts are in solution, and add 50 ml. of boiling water. Add 10 ml. of cinchonine solution and let stand overnight. Filter and wash with cinchonine wash solution.

(c) Evaporate the filtrate and washings until a slight film begins to form and complete the determination as described in Section 1 (b) to (g). In this determination, the correction for a blank determination is particularly important. As the cinchonine solution may contain sulfur, this solution should be measured so that exactly the same amount is used in the blank as in the determination.

**4. Open-Hearth Iron, Cast Iron, Wrought Iron, and High-Silicon Steels.**—Determine sulfur in accordance with the procedure described in Section 1.

## THE EVOLUTION METHOD

**Apparatus.**—The apparatus shown in Fig. 24-6 may be used for determining sulfur by the evolution method in testing materials that are soluble in HCl (1:1). It should consist of a 300-ml. Florence flask fitted with a "sulfur-free" two-hole rubber stopper carrying a thistle tube and a second glass tube dipping into a beaker containing ammoniacal  $\text{ZnSO}_4$  or  $\text{CdCl}_2$  solution.

The apparatus shown in Fig. 24-7 is recommended for the analysis of materials when concentrated acid is used for solution and maintenance of the acid's strength by means of condensation is desirable.<sup>41</sup> In this apparatus hydrogen supplied from a Kipp generator or a cylinder of hydrogen is freed from  $\text{H}_2\text{S}$  by passage through  $\text{KMnO}_4$  (25 g. per liter) contained in a Drechsel bottle *B* of about 125-ml. capacity, and NaOH (300 g. per liter) held in another Drechsel bottle *C* of the same size. The tube *G* dips just beneath the surface of 25 ml. of cold water held in the 125-ml. Erlenmeyer flask *H*. The water serves to collect the HCl that distills

<sup>41</sup> It is advisable to use an all-glass apparatus because the length of time (30 min.) required for the solution of the material gives opportunity for fumes of HCl to attack rubber stoppers and rubber hose connections, which usually contain sulfur, and thus cause erroneous results.

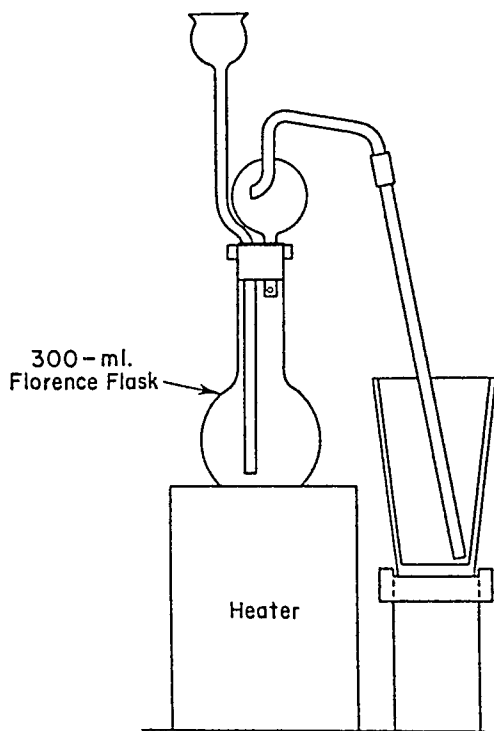


FIG. 24-6. Apparatus for Determination of Sulfur by Evolution Method.

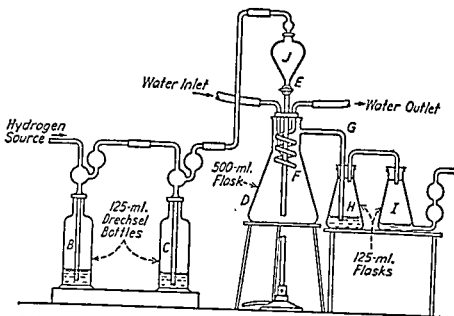


FIG. 24-7. Apparatus for Determination of Sulfur by Evolution Method.

over, and to prevent the absorbent solution in *I* from becoming acid. Hydrogen is admitted through the glass stopcock *E* to the 500-ml. decomposition flask *D*. The decomposition flask (Pulsifers' design) shall be provided with a ground glass stopcock *E*, a funnel *J*, and a cooling coil *F*, with inlet and outlet tubes. An ammoniacal solution of  $\text{CdCl}_2$  or  $\text{ZnSO}_4$  shall be held in the 125-ml. absorption flask *I*. If the  $\text{CdCl}_2$  solution is used, the absorption should not be carried out in direct sunlight.

**Reagents.** (a) **Ammoniacal Zinc Sulfate Solution.**—Dissolve 200 g. of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in 1 liter of water, and add 1 liter of  $\text{NH}_4\text{OH}$ . Let stand 24 hr. and filter.

(b) **Starch Solution.**—To 500 ml. of boiling water, add a cold suspension of 5 g. of soluble (or arrowroot) starch in 25 ml. of water. Cool, and add a cool solution of 5 g. of  $\text{NaOH}$  in 50 ml. of water. Add 15 g. of  $\text{KI}$  and mix thoroughly.

(c) **Standard Potassium Iodate Solution (0.03 N).**—For general work, use the theoretical sulfur equivalent of this solution. For specialized work on one kind of material, the solution may be standardized against like material by carrying 5 g. portions of the proper standard through all steps of the corresponding procedure (see Sections 1 to 4).

**Procedure. 1. Carbon Steels.**—(a) Transfer 5 g. of the sample to a dry, 300 ml. Florence flask and assemble the apparatus as illustrated (Fig. 24-6). Place 15 ml. of ammoniacal  $\text{ZnSO}_4$  solution and 200 ml. of water in the beaker. Add 80 ml. of  $\text{HCl}$  (1:1) to the flask through the thistle tube, heat the flask and its contents gently until the solution of the iron is complete, then boil the solution for 30 sec. The heat shall be so adjusted that there is a rapid, steady evolution of gas.<sup>42</sup>

(b) Disconnect the delivery tube, leaving it in the solution, and remove the beaker. Add 2 ml. of starch solution, then 40 ml. of  $\text{HCl}$  (1:1), and titrate immediately with 0.03 N  $\text{KIO}_3$  to a permanent blue color.

<sup>42</sup> This method is most satisfactory when the evolution of gas is rapid and the conditions are kept constant. Trouble may occur if the absorbing solution becomes too hot. This condition can be avoided by keeping the absorbing solution in a water bath.

(c) **Calculation.**—Calculate the percentage of sulfur as follows:

$$\text{Sulfur, per cent} = \frac{AB \times 0.016}{C} \times 100$$

where  $A$  = milliliters of  $\text{KIO}_3$  solution required for titration of the sample,

$B$  = normality of the  $\text{KIO}_3$  solution, and

$C$  = grams of sample used.

(d) With most carbon steels, the results for sulfur that are obtained by the evolution method and the use of the theoretical sulfur equivalent agree with the gravimetric results within plus or minus 0.002%. Some steels dissolve too slowly and some (for example, certain steels containing high sulfur or high carbon) do not yield all their sulfur. In such cases the samples must be annealed as follows: Place 5 g. of the sample in a 20-ml. porcelain crucible. Cover with a  $\frac{1}{4}$ -in. layer of powdered or flake graphite, cover the crucible, and heat at  $685^\circ\text{C}$ . for 20 min. Transfer the cooled annealed steel and graphite to the evolution flask and proceed in accordance with Paragraphs (a) to (c).

**2. Alloy and High-Silicon Steels.**—Many alloy steels yield all their sulfur when analyzed by the same procedure as is used for carbon steels, but some yield only a part. Hydrochloric acid (2:1) or concentrated  $\text{HCl}$  will give slightly more evolved sulfur, with some alloy steels, than does  $\text{HCl}$  (1:1). For example, some molybdenum steels yield most of their sulfur with concentrated  $\text{HCl}$ . For high-silicon steels, concentrated  $\text{HCl}$  plus a small amount of  $\text{HF}$  (0.5 ml.) has been recommended. The evolution method, however, can be used only if experiment has shown that all sulfur is evolved as  $\text{H}_2\text{S}$  in the particular type of steel under analysis. The evolution method is not satisfactory for the determination of sulfur in selenium steels. When concentrated  $\text{HCl}$  is used, suitable condensing arrangements must be provided (see Fig. 2-4-7).

**3. Cast Iron.**—(a) Most cast irons do not give up all their sulfur as  $\text{H}_2\text{S}$ . The amount that is given off can often be increased by annealing the sample, although with many irons annealing yields no increase in the amount of evolved sulfur. Annealing is done as described in Paragraph (d) above.

(b) With high-silicon cast irons, use hot ( $70^\circ\text{C}$ .)  $\text{HCl}$  (1:1), heat rapidly to boiling, and then simmer. If the solution froths badly, add about 0.5 ml. of  $\text{HF}$ .

(c) Concentrated  $\text{HCl}$  has been recommended for certain alloy cast irons, in which case suitable condensing arrangements must be provided. Even then care must be taken to avoid excessive neutralization of the alkaline absorbent.

**4. Open-Hearth Iron and Wrought Iron.**—Determine sulfur in accordance with the procedure described in Section 1.

## THE DIRECT COMBUSTION-IODATE METHOD <sup>43</sup> (E30-60T) (FOR STAINLESS STEELS)

**Apparatus.**—The apparatus shall be suitable for the direct combustion of the metal in oxygen, the  $\text{SO}_2$  obtained being absorbed in starch-iodide solution and

<sup>43</sup> The combustion method for the determination of sulfur is especially useful for stainless steels that do not react satisfactorily in the evolution method described in Sections 1 to 4. In this method, a minimum furnace temperature of  $1425^\circ\text{C}$ . is prescribed. It has been found that at this temperature most stainless steels will yield approximately 93% of their sulfur content as  $\text{SO}_2$ . One empirical factor for the  $\text{KIO}_3$  solution is, therefore, employed instead of a series of factors varying with the temperature of combus-



titrated with standard  $\text{KIO}_3$  solution. A typical arrangement is shown in Fig. 24-8.

(a) **Combustion Furnace.**—Any electric tube-furnace capable of continuous operation at  $1425^\circ\text{C}$ ., and intermittently up to  $1525^\circ\text{C}$ ., is suitable. The combustion zone shall be approximately 8 to 10 in. in length. Furnaces utilizing rod shape silicon carbide heating elements are satisfactory.

(b) **Temperature Control.**—To insure maximum reproducibility of results, it is necessary that reasonably close regulation of the furnace temperature be employed. This is best accomplished by means of an automatic controller, although other suitable means may be used.

(c) **Combustion Tube.**—The tube shall be of a refractory type that will withstand a temperature of  $1400^\circ$  to  $1550^\circ\text{C}$ . It shall have an internal diameter of  $\frac{7}{8}$  to  $1\frac{1}{4}$

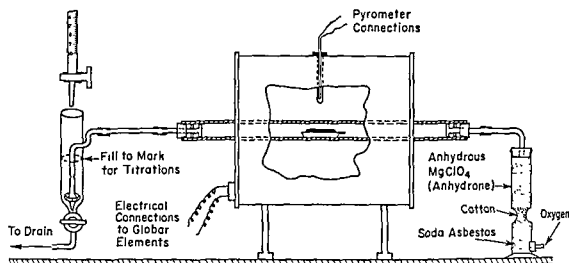


FIG. 24-8. Typical Arrangement for Determination of Sulfur by the Direct-Combustion Method.

in. and a length of about 27 to 36 in. The tube shall be placed in the furnace so that the exit end extends approximately 5 in. beyond the furnace.

(d) **Combustion Boats and Covers.**—Refractory boats of very low sulfur content, resistant to molten iron oxide, and about 3.5 to 4 in. in length are recommended. Prior to use, boats and covers shall be ignited in oxygen at or above the operating temperature for 15 to 20 min. in order to remove traces of sulfur. After ignition, both boats and covers shall be stored in moisture-free glass-stoppered containers.

(e) **Oxygen Purifiers.**—The regular commercial tank oxygen is satisfactory. It shall be passed through an absorption tower containing an absorbent such as a 20 to 30-mesh inert base impregnated with  $\text{NaOH}$  <sup>44</sup> and then through a tower containing anhydrous  $\text{Mg}(\text{ClO}_4)_2$ . A large reservoir (such as a 5- to 10-l. bottle) shall be inserted between the oxygen-purifying towers and the inlet of the combustion tube. A reservoir provides a more even flow of oxygen during the fusion period. **Caution.**—The reservoir bottle must be dry and free of all organic compounds or vapors to avoid the formation of explosive mixtures with oxygen.

(f) **Absorption and Titration Apparatus.**—A number of types of apparatus for

tion and type of stainless steel being analyzed. Though the direct combustion iodate procedure for determining sulfur in stainless steels is empirical, close adherence to the details of the method will yield results of suitable reproducibility and accuracy.

<sup>44</sup>Ascarite and Caroxite have been found satisfactory for this purpose.

absorption and titration are commercially available. Suitable apparatus may be built in the laboratory.

(g) **Rubber and Glass Connections.**—The rubber stoppers at the inlet and outlet ends of the combustion tube shall be protected by heat-reflecting baffles, preferably of the double-disc type. Connection between the outlet end of the combustion tube and the absorption and titration vessel shall be made with glass, butted to minimize areas of rubber tubing exposed to the gases. The length of the glass tubing is not critical. A convenient length to use is 10 in. After each 8 hr. of continuous use, the glass tubing shall be thoroughly dried by heating with a burner. The rubber stoppers and tubing used shall be essentially free of sulfur.

**Reagents.** (a) **Starch Solution.**—Transfer 9 g. of soluble (or arrowroot) starch to a small beaker, add 5 to 10 ml. of water, and stir until a smooth paste is obtained. Pour the mixture slowly into 500 ml. of boiling water. Cool, add 15 g. of KI, and stir until the KI is dissolved. Dilute to 1 liter.

(b) **Standard Potassium Iodate Solution** (1 ml. = 0.0001 g. S).<sup>45</sup>—Dissolve 0.2069 g. of  $\text{KIO}_3$  in 900 ml. of water and dilute to 1 liter in a volumetric flask.

**Procedure.**—(a) For type 302 (18 Cr, 8 Ni) stainless steel, adjust the temperature of the furnace to 1425°C. For type 308 (19 Cr, 10 Ni) stainless steel use a furnace temperature of 1465°C., and for type 310 (24 Cr, 19 Ni) stainless steel use 1525°C.

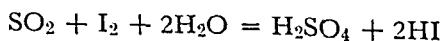
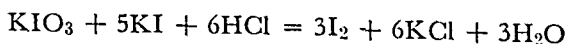
(b) Add about 65 to 70 ml. of HCl (3:197) and 2 ml. of starch solution to the absorption vessel. Pass oxygen<sup>46</sup> through the system and add a small amount of  $\text{KIO}_3$  (1 ml. = 0.0001 g. S) until the intensity of the blue color is that which is to be taken as the end point in the final titration. Read the buret and record as the initial reading. Turn off the oxygen.

(c) Transfer 1 g. (0.2 g. for high-sulfur steels) of the sample to a preignited combustion boat, spreading the chips evenly over about one-half the length of the boat. Cover the sample with approximately 0.2 g. of fine copper turnings or, preferably, with a sheet of copper foil. Place a preignited cover on the boat and introduce the boat and contents into the center of the combustion zone of the combustion tube. Close the tube and allow the sample to heat for 1.5 min.; then start the flow of oxygen at a rate of approximately 1500 ml. per min.

(d) As the stream of gas begins to bubble through the absorption solution, the blue color will fade. Titrate continuously with  $\text{KIO}_3$  (1 ml. = 0.0001 g. S) at such a rate as to maintain, as nearly as possible, the initial intensity of the blue color. Near the end of the 10-min. combustion period, cautiously add  $\text{KIO}_3$  (1 ml. = 0.0001 g. S) until the intensity of the blue color is that taken initially (Paragraph (b)). Read the buret and record the reading. Subtract the initial reading (Paragraph (b)). The difference is the milliliters of  $\text{KIO}_3$  solution required for titration of the sample.

(e) **Blank.**—Make a blank determination, following the same procedure and using the same amounts of all reagents.

<sup>45</sup> This sulfur equivalent is based on the following:



On the basis of 93% conversion of sulfur to  $\text{SO}_2$ ,

$$0.2225 \times 0.93 = 0.2069 \text{ g. of } \text{KIO}_3 \text{ per liter.}$$

One milliliter of the  $\text{KIO}_3$  solution is therefore equivalent to 0.0001 g. of sulfur.

<sup>46</sup> The regular commercial tank oxygen is satisfactory for this purpose.

(f) Calculation.—Calculate the percentage of sulfur as follows:

$$\text{Sulfur, per cent} = \frac{(A - B) \times 0.0001}{C} \times 100$$

where  $A$  = milliliters of  $\text{KIO}_3$  solution required for titration of the sample,  
 $B$  = milliliters of  $\text{KIO}_3$  solution required for titration of the blank, and  
 $C$  = grams of sample used.

## SELENIUM

### THE SULFUROUS ACID-IODOMETRIC METHOD

*Reagents.* (a) Sulfurous Acid (6%).

(b) Urea.

(c) Potassium Iodide Solution (300 g. per liter).—Prepare fresh as required.

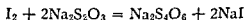
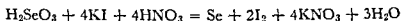
(d) Starch Solution (50 g. per liter).—Make a paste of 5 g. of soluble (or arrow-root) starch in about 5 ml. of water and add this to 100 ml. of boiling water. Cool before using. Prepare fresh as required.

(e) Standard Selenious Acid Solution (1 ml. = 0.0006 g. Se).—Dissolve 0.490 g. of selenious acid ( $\text{H}_2\text{SeO}_3$ ) in 400 ml. of water and dilute to 500 ml. in a volumetric flask.

(f) Standard Sodium Thiosulfate Solution (1 ml. = 0.0002 g. Se. approximately 0.01 N).—Dissolve 2.5 g. of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in 1 liter of freshly boiled and cooled water. Standardize as follows: Pipet 10 ml. of the selenious acid solution into a 600-ml. beaker. Add 20 ml. of  $\text{HNO}_3$  and boil until the volume is about 15 ml. Cool, dilute to 400 ml., add 2 g. of urea, and stir. Add 10 ml. of KI (300 g. per liter), stir, and allow to stand for 2 min. Add 5 ml. of starch solution (50 g. per liter), and titrate with the  $\text{Na}_2\text{S}_2\text{O}_3$  solution until the blue color is discharged. Calculate the selenium equivalent of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution in grams per milliliter, as follows:

$$\text{Selenium equivalent} = \frac{0.006}{\text{ml. of } \text{Na}_2\text{S}_2\text{O}_3}$$

The reactions involved are:



The  $\text{Na}_2\text{S}_2\text{O}_3$  solution may also be standardized against  $\text{KIO}_3$  and the selenium equivalent calculated on the theoretical basis. One milliliter of 1 N  $\text{Na}_2\text{S}_2\text{O}_3$  is equivalent to 0.01974 g. of selenium.

*Procedure.* 1. *Stainless Steels.*—(a) Transfer 5 g. of the sample (use 2 to 3 g. of the sample if the selenium content is over 0.2%) to a 600-ml. beaker, and add a freshly prepared mixture of 30 ml. of  $\text{HNO}_3$  and 30 ml. of  $\text{HCl}$ . Heat until action is complete. Add 35 ml. of  $\text{HClO}_4$  and heat until chromium is oxidized, which is indicated by the appearance of a deep red color in the solution. Cool, add 50 ml. of water, and warm until salts are dissolved. Add 200 ml. of  $\text{HCl}$  and 100 ml. of  $\text{H}_2\text{SO}_3$  (6%), and heat on a steam bath at  $60^\circ$  to  $70^\circ\text{C}$ . for 2 to 3 hr., to reduce the selenium to the metallic state. Cool, and filter with suction through a tight asbestos pad in a Gooch crucible having a removable bottom, or through a fritted-

glass crucible of fine porosity. Wash 5 or 6 times with cold HCl (3:7) and then 5 or 6 times with cold water.

(b) Transfer the asbestos pad with the residue to a 400-ml. beaker, add 50 ml. of  $\text{HNO}_3$ , and evaporate the solution to 10 to 15 ml. Filter by suction through a Gooch crucible or a fritted-glass crucible of fine porosity, and wash several times with cold water. If the filtrate is cloudy, filter again. Add a slight excess of  $\text{NH}_4\text{OH}$  to precipitate small amounts of iron. Filter and wash with warm water.

(c) Make the filtrate just acid with  $\text{HNO}_3$  and add 10 ml. in excess. Dilute to 400 ml., heat to  $60^\circ\text{C}$ ., add 3 g. of urea, and stir 2 or 3 min. to eliminate small amounts of  $\text{HNO}_2$ . Cool, add 10 ml. of KI (300 g. per liter), and allow to stand until the liberation of iodine is complete (usually 2 or 3 min.). Add 5 ml. of starch solution (50 g. per liter) and titrate with  $\text{Na}_2\text{S}_2\text{O}_3$  (1 ml. = 0.0002 g. Se) to the complete disappearance of the blue color.

(d) **Calculation.**—Calculate the percentage of selenium as follows:

$$\text{Selenium, per cent} = \frac{AB}{C} \times 100$$

where  $A$  = milliliters of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required to titrate the sample,

$B$  = selenium equivalent of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution, in grams per milliliter, and

$C$  = grams of sample used.

## SILICON

### THE SULFURIC ACID METHOD

**Reagents. Mixed Acids.**—To 600 ml. of water add 200 ml. of  $\text{H}_2\text{SO}_4$ , 100 ml. of  $\text{HNO}_3$ , and 100 ml. of HCl.

**Procedure. 1. Carbon and High-Silicon Steels.**—(a) Transfer the sample (5 g. if silicon is under 0.5%, and 2.5 g. if it is over this percentage) to a 300-ml. casserole, add 100 ml. of  $\text{H}_2\text{SO}_4$  (1:4),<sup>47</sup> and cover. Warm gently. When reaction ceases, remove and rinse the cover and evaporate the solution to dense white fumes, taking care to avoid spattering. Replace the cover and continue the fuming for 2 to 3 min., but no longer, since insoluble sulfates may be formed. Cool somewhat, and add 100 ml. of warm water ( $40^\circ$  to  $50^\circ\text{C}$ .) at one time. Stir until salts are in solution, heating gently if necessary, but never boiling. Filter immediately, using a rapid ashless filter paper for high-silicon steels, and a tighter paper for low-silicon steels. Transfer all the residue to the paper, scrubbing the casserole thoroughly with a rubber-tipped rod. Wash the paper and residue alternately with hot HCl (5:95) and hot water until iron salts have been removed. This usually requires six washings with 5-ml. portions of each wash liquid.<sup>48</sup>

<sup>47</sup> More rapid and equally satisfactory determinations can be made by dissolving the sample in 40 ml. of HCl (1:1) and evaporating to low volume; then adding the  $\text{H}_2\text{SO}_4$ , evaporating to fumes, and completing the procedure in accordance with Section 1 above. Alternatively, the sample may be dissolved in 100 ml. of the mixed acids as described below in Section 6. In the case of steels (rimming) containing under 0.10% silicon, dissolve the sample in a platinum dish with HCl, add  $\text{H}_2\text{SO}_4$ , and evaporate to fumes and complete the determination as directed in Section 1.

<sup>48</sup> In this method and succeeding methods for determining silicon some silica passes into the filtrate. The amount left in solution depends chiefly on the silicon content of the alloy, that is, about 0.005% silicon for a 0.1% silicon steel, approximately 0.02% for a 0.4% silicon steel, and about 0.05% or over for a 4.5% silicon steel. Hence in umpire work it is necessary to evaporate the filtrate and washings to dense white fumes, dilute, filter, and ignite the washed paper and contents with the first portion.

(b) Transfer the paper and residue to a platinum crucible, heat carefully until the carbon is gone, and then cover and ignite for 30 min. at 1100° to 1150°C. Cool in a desiccator and weigh.

(c) Add enough  $\text{H}_2\text{SO}_4$  (1:1) to moisten the  $\text{SiO}_2$  and then 3 to 5 ml. of  $\text{HF}$ . Evaporate to dryness, carefully heat until  $\text{H}_2\text{SO}_4$  is gone, and then ignite at 1000°C. Cool in a desiccator and weigh. The loss in weight represents  $\text{SiO}_2$ .

(d) Calculation.—Calculate the percentage of silicon as follows:

$$\text{Silicon, per cent} = \frac{A \times 0.4675}{B} \times 100$$

where  $A$  = grams of  $\text{SiO}_2$ , and

$B$  = grams of sample used.

**2. Alloy Steels.**—Determine silicon in accordance with the procedure described in Section 1, if the sample dissolves in  $\text{H}_2\text{SO}_4$  (1:4). If it does not, use the mixed acids<sup>47</sup> or the perchloric acid method. The perchloric acid method is especially suited for high-chromium alloys.

**3. Tungsten Steels.**—(a) Transfer 2.5 g. of the sample to a beaker or casserole provided with a cover glass. Add a mixture of 20 ml. of  $\text{HCl}$  and 20 ml. of  $\text{HNO}_3$ , and warm until all the steel has dissolved. Add 60 ml. of warm  $\text{H}_2\text{SO}_4$  (1:1), and evaporate to dense white fumes. Cool somewhat, cautiously add 5 ml. of  $\text{HCl}$ , and swirl gently until well mixed. Add 125 ml. of warm water (40° to 50°C.), and proceed as described in Section 1 (a).

(b) Ignite the tungstic acid and silica together at a temperature of about 1000°C. and weigh.

(c) Complete the determination as described in Section 1 (c) and (d), except that the final ignition shall be made at 800°C. instead of 1000°C.

**4. Cast Iron.**—Determine silicon in accordance with the procedure described in Section 1, using 2.5 g. of the sample. With gray or mottled pig iron it is desirable to use a finely divided sample and to boil vigorously with slightly more acid at the start, as the particles tend to become coated with silicic acid. Alternatively, the sample (2.5 g.) may be dissolved in 80 ml. of the mixed acids as described in Section 6.

**5. Open-Hearth Iron.**—Determine silicon in accordance with the procedure described in Section 1, using 10 to 20 g. of the sample and corresponding amounts of  $\text{H}_2\text{SO}_4$ . Fume gently for 12 to 15 min., instead of 1 to 2 min. as with carbon steels. The solution and treatment of the sample shall be carried out in a platinum dish.

**6. Wrought Iron.**—To 5 g. of the sample, add 100 ml. of the mixed acids. Heat until solution is complete, evaporate to dense white fumes, and fume for 1 to 2 min. Cool somewhat, and cautiously add to the warm solution 5 ml. of  $\text{HCl}$ , while swirling the solution gently. When well mixed, add 125 ml. of warm water, stir, and complete the determination as described in Section 1.

## THE PERCHLORIC ACID METHOD

**Procedure.** **1. Carbon and High-Silicon Steels.**—Transfer 5 g. of the sample for steels containing less than 0.5% silicon and 2.5 g. for steels containing more than 0.5% silicon to a 400-ml. beaker. Add 40 ml. of  $\text{HNO}_3$  (3:5).<sup>48</sup> Cover and heat

<sup>48</sup> For high-silicon alloys, dissolve the sample in 40 ml. of  $\text{HCl}$  (1:1), oxidize carefully with  $\text{HNO}_3$ , and then add the  $\text{HClO}_4$ .

cautiously until solution is complete. Then raise the cover and add 40 ml. of  $\text{HClO}_4$  for the 2.5-g. sample, or 60 ml. for the 5-g. sample. Evaporate to white fumes, cover the beaker, and continue to heat at such a rate that  $\text{HClO}_4$  refluxes on the sides of the beaker for 15 to 20 min. Cool somewhat, add 125 ml. of hot water, and stir until salts are in solution, crushing any lumps of silica with a flattened rod. Filter immediately and complete the determination as described in Section 1. The washing of the paper must be thorough, for residual  $\text{HClO}_4$  held in the silicic acid tends to cause popping and loss of material upon subsequent ignition.

**2. Nickel, Chromium-Nickel, Chromium-Vanadium, and Similar Low-Alloy Steels Containing No Tungsten and Under 5% Chromium.**—Determine silicon in accordance with the procedure described in Section 1.

**3. High-Chromium Steels.**—Dissolve the sample in a mixture of equal parts of  $\text{HCl}$  and  $\text{HNO}_3$ . Complete the determination as described in Section 1.

**4. Cast Iron.**—Determine silicon in accordance with the procedure described in Section 1, using 2.5 g. of the sample for white iron and 1 g. for gray iron.

**5. Alloy Cast Iron.**—For high chromium-nickel cast iron dissolve the sample in a mixture of 20 ml. of  $\text{HCl}$  and 20 ml. of  $\text{HNO}_3$ . Complete the determination as described in Section 1.

## COPPER

### THE ELECTROLYTIC OR GRAVIMETRIC METHOD

**Apparatus. Electrodes.**—Platinum electrodes of the stationary type as described in the following Paragraphs (a) and (b). are recommended, but strict adherence to the exact size and shape of the electrodes is not mandatory. Where agitation of the electrolyte is permissible in order to decrease the time of deposition, one of the types of rotating forms of electrodes, generally available, may be employed.

(a) **Cathodes.**—Platinum cathodes may be formed either from plain or perforated sheets or from wire gauze, and may be either open or closed cylinders. Gauze cathodes are recommended, and shall be made preferably from gauze containing approximately 400 meshes per sq. cm. (50 meshes per linear inch). Gauze for cathodes shall be woven from wire of approximately 0.0085 in. (0.21 mm.) in diameter. The cathode should be stiffened by doubling the gauze for about 3 mm. at the top and the bottom of the cylinder or by reinforcing the gauze at the top and bottom with a platinum band or ring. The cylinder should be approximately 30 mm. in diameter and 50 mm. in height. The stem should be made from a platinum alloy wire, such as platinum-iridium, platinum-rhodium, or platinum-ruthenium, having a diameter of approximately 1.30 mm. It should be flattened and welded the entire length of the gauze. The over-all height of the cathode should be approximately 130 mm. Cathodes should be sandblasted.

(b) **Anodes.**—Platinum anodes may be of the spiral type when anodic deposits are not being determined, or if the deposits are small (as in the electrolytic determination of lead when it is present in amounts not over 0.2%). When used in analyses where both cathodic and anodic plates are to be determined, the anodes should be of wire gauze. Spiral anodes should be made from 1.00-mm. or larger platinum wire formed into a spiral of seven turns having a height of approximately 50 mm. and a diameter of 12 mm., the over-all height being approximately 130 mm. The spiraled section should be sandblasted. Platinum gauze anodes should be

made of the same material and of the same general design as platinum gauze cathodes. The anode cylinder should be approximately 12 mm. in diameter and 50 mm. in height and the over-all height of the anode should be approximately 130 mm. Platinum gauze anodes should be sandblasted.

**Reagents.** Hydrogen Sulfide Wash Solution.—Saturate  $\text{H}_2\text{SO}_4$  (1:99) with  $\text{H}_2\text{S}$ .

**Procedure.** 1. *Copper Steels.*—(a) Transfer 5 g. of the sample to a 600 ml beaker, add 200 ml. of  $\text{H}_2\text{SO}_4$  (1:9), and heat gently until action ceases. Dilute to 350 ml. with water, heat to boiling, and saturate with  $\text{H}_2\text{S}$  as the solution is allowed to cool during the course of 25 min. Allow the precipitate to settle, filter on paper or paper pulp, and wash a few times with  $\text{H}_2\text{S}$  wash solution.

(b) Transfer the residue and paper to a 25- or 35-ml. tall-form porcelain crucible, ignite at a temperature not exceeding  $550^\circ\text{C}.$ , and fuse with 2 to 4 g. of  $\text{K}_2\text{S}_2\text{O}_7$ . Dissolve the cooled melt in 25 ml. of  $\text{HCl}$  (1:9). Dilute the solution to 100 ml.,<sup>50</sup> neutralize with  $\text{NaOH}$  (50 g. per liter), and add approximately 0.3 ml. in excess. Boil for 3 min., digest for about 30 min., filter, and wash 5 or 6 times with cool  $\text{NaOH}$  (5 g. per liter).

(c) Dissolve the precipitate in 15 to 25 ml. of hot  $\text{HNO}_3$  (1:3), wash the paper with hot water, add 5 ml. of  $\text{H}_2\text{SO}_4$ , and evaporate to dense white fumes. Cool the solution, dilute to 40 ml., add an excess of several milliliters of  $\text{NH}_4\text{OH}$ , and heat to boiling. Allow the precipitate to settle, filter into a 250-ml. beaker, and wash with hot water. If more than 4 mg. of iron, tin, chromium, or other elements precipitable by  $\text{NH}_4\text{OH}$  appear to be present, dissolve the precipitate in 15 to 25 ml. of hot  $\text{HNO}_3$  (1:3) and repeat the precipitation with  $\text{NH}_4\text{OH}$ . Filter and combine the filtrates.

(d) Complete the determination by the electrolytic method (Paragraphs (e) to (g)) or the gravimetric method (Paragraphs (h) to (j)). The electrolytic method is to be preferred in analyses of the highest accuracy, and if over 0.25% of copper is present.

**Electrolytic Method.**—(e) Transfer the ammoniacal solution (Paragraph (c)) to a 250-ml. beaker, neutralize with  $\text{H}_2\text{SO}_4$  (1:1), add an excess of 5 ml. of  $\text{H}_2\text{SO}_4$  (1:1), and then add 4 ml. of  $\text{HNO}_3$  (1:1). Dilute the solution to 200 ml. Adjust the anode and weighed cathode, cover the beaker with split watch glasses, and electrolyze at a current density of 0.5 amp. per sq. dm. until the solution becomes colorless (about 2 hr.). Rinse the cover glasses and the exposed stems of the electrodes and sides of the beaker. Continue the electrolysis for 30 min. and test for complete deposition (0.3 to 0.5 ml. of the electrolyte should not give a brown color with 0.3 to 0.5 ml. of freshly prepared  $\text{H}_2\text{S}$  water).

(f) When deposition of the copper is complete, lower the electrolytic beaker quickly, with the current still on, while rinsing the cathode with water from a wash bottle.<sup>51</sup> Turn off the current, quickly detach the cathode and rinse it in a beaker of water, and then dip it in two successive baths of ethanol or methanol. Dry in an oven at  $110^\circ\text{C}.$  for 3 to 5 min., cool in a desiccator, and weigh the deposit as metallic copper.<sup>52</sup>

<sup>50</sup> If an appreciable amount of silica has separated, it may be removed by filtration before proceeding further.

<sup>51</sup> In work of high accuracy, recover traces of copper in the electrolyte by the sulfide-colorimetric method.

<sup>52</sup> Deposits of copper may be removed by immersing the cathode in  $\text{HNO}_3$  (1:1), rinsing with water, then boiling with fresh  $\text{HNO}_3$  for 5 to 10 min., rinsing with water, and then igniting strongly for 10 to 25 min. over one or two large Meker burners.

(g) **Calculation.**—Calculate the percentage of copper as follows:

$$\text{Copper, per cent} = \frac{A}{B} \times 100$$

where  $A$  = grams of  $\text{CuO}$ , and  
 $B$  = grams of sample used.

**Gravimetric Method (Copper Under 0.25%).**—(h) Neutralize the ammoniacal solution (Paragraph (c)) with  $\text{H}_2\text{SO}_4$  (1:1), add 4 ml. in excess, and adjust the volume to about 100 ml. Heat to boiling, and saturate with  $\text{H}_2\text{S}$  as the solution cools. Allow to settle and filter. Transfer all the precipitate to the paper, and wash thoroughly with  $\text{H}_2\text{S}$  wash solution.

(i) Transfer the paper and precipitate to a small porcelain or quartz crucible that has been weighed with cover. Heat under good oxidizing conditions until carbon has been destroyed, and then ignite to constant weight at  $900^\circ$  to  $1000^\circ\text{C}$ . Cover, cool over a good desiccant, and weigh as  $\text{CuO}$ .

(j) **Calculation.**—Calculate the percentage of copper as follows:

$$\text{Copper, per cent} = \frac{A \times 0.799}{B} \times 100$$

where  $A$  = grams of copper, and  
 $B$  = grams of sample used.

**2. Carbon Steels.**—Determine copper in accordance with the procedure described in Section 1, using 10 g. of the sample.

**3. Alloy Steels.**—Most alloy steels may be analyzed as described in Section 1.

**4. Tungsten Steels.**—(a) To 5 g. of the sample, add 100 ml. of  $\text{HCl}$  (1:1), and heat gently until the sample has dissolved. Carefully add 20 ml. of  $\text{HNO}_3$  (1:1), and boil gently until the tungstic acid becomes bright yellow. Dilute the solution to 150 ml. with boiling water, digest for a few minutes, filter, and wash with  $\text{HCl}$  (1:9). Reserve the residue.

(b) Add 15 ml. of  $\text{H}_2\text{SO}_4$  to the filtrate, evaporate just to white fumes, cool, and add 100 ml. of water. If a small residue of tungstic acid separates, filter, and wash with  $\text{H}_2\text{SO}_4$  (5:95). Add 5 g. of tartaric acid to the clear filtrate, neutralize with  $\text{NH}_4\text{OH}$ , adjust the acidity to 5% by volume with  $\text{H}_2\text{SO}_4$ , heat to boiling, and pass a rapid stream of  $\text{H}_2\text{S}$  into the solution for 10 to 15 min. Let the precipitate settle, filter, and wash with  $\text{H}_2\text{S}$  wash solution.

(c) Add  $\text{NH}_4\text{OH}$  to the residue (Paragraph (a)), add 5 g. of tartaric acid, and then add sufficient  $\text{H}_2\text{SO}_4$  to have an excess of 5 ml. per 100 ml. of solution. Pass  $\text{H}_2\text{S}$  into the solution until precipitation is complete, filter, and combine with the main sulfide precipitate (Paragraph (b)).

(d) Complete the determination as described in Section 1 (b) to (j).

**5. Cast Iron and High-Silicon Steels.**—(a) Dissolve 5 g. of the sample in 100 ml. of  $\text{H}_2\text{SO}_4$  (1:5). When solution is complete, evaporate to dense white fumes. Cool somewhat, dilute to 100 ml. with warm water, heat until salts have dissolved, and filter.

(b) Wash the residue with hot water and ignite in platinum at a temperature not exceeding  $550^\circ\text{C}$ . Add 2 ml. of  $\text{H}_2\text{SO}_4$  (1:1) and 3 to 5 ml. of  $\text{HF}$ , evaporate to dense white fumes, cool and add to the main filtrate. Dilute the filtrate to 500 ml. with hot water, and complete the determination as described in Section 1.

**6. Wrought Iron and Open-Hearth Iron.**—Determine copper in accordance with the procedure described in Section 1, using 10 g. of the sample.



## THE THIOSULFATE-IODIDE METHOD

**Reagents.** (a) Sodium Thiosulfate Solution (500 g. per liter).—Filter, if not clear, before using.

(b) Hydrogen Sulfide Wash Solution.—Saturate  $\text{H}_2\text{SO}_4$  (1:99) with  $\text{H}_2\text{S}$ .

(c) Ammonium Bifluoride Solution (200 g. per liter).

(d) Standard Sodium Thiosulfate Solution (1 ml. = 0.001 g. Cu, approximately 0.02 N).—To standardize, transfer 0.05 g. of copper to a 150-ml. beaker, cover, and dissolve the copper in 4 to 5 ml. of  $\text{HNO}_3$  (3:5). Boil gently until brown fumes have been expelled. Cool, and add  $\text{NH}_4\text{OH}$  until the solution just turns blue. Acidify with acetic acid and add 1 ml. in excess. Continue as described in Section 1 (c) below.

(e) Starch Solution.

**Procedure. 1. Copper Steels.**—(a) Transfer 5 g. of the sample to a 600-ml. beaker, add 100 ml. of  $\text{H}_2\text{SO}_4$  (1:9), and heat gently until action ceases. Dilute to 250 ml., heat to boiling, add 10 ml. of  $\text{Na}_2\text{S}_2\text{O}_3$  (500 g. per liter), and continue the boiling for 5 to 10 min., or until the precipitate settles rapidly. Filter immediately, transfer all the precipitate to the paper, and wash the paper and precipitate well with  $\text{H}_2\text{S}$  wash solution.

(b) Place the paper and precipitate in a porcelain or silica crucible, dry, and ignite at a low temperature ( $520^\circ$  to  $550^\circ\text{C}$ .; conveniently in a muffle furnace) until all carbon is destroyed. Cool and transfer the contents of the crucible to a 250 ml. beaker. Add 5 to 6 ml. of  $\text{HNO}_3$  (3:5) to the crucible, warm gently, and pour upon the residue in the beaker. Rinse the crucible with a little water and warm the beaker and contents until the copper oxide has dissolved. Carefully evaporate the solution to a volume of 2 to 3 ml. in order to expel most of the acid. Cool, add 30 ml. of water,<sup>53</sup> and add either 5 ml. of  $\text{NH}_4\text{HF}_2$  solution (200 g. per liter) or 1 g. of NaF to prevent interference by ferric iron. Then add  $\text{NH}_4\text{OH}$  until the solution just reacts alkaline to litmus. Cool the solution to room temperature. Acidify with acetic acid and add 1 ml. in excess.

(c) Add 3 to 4 g. of KI dissolved in a little water, stir well, and immediately titrate with  $\text{Na}_2\text{S}_2\text{O}_3$  (1 ml. = 0.001 g. Cu). When the brown tint has nearly disappeared, add 5 ml. of starch solution and continue the titration until one drop changes the color from blue to yellowish white, persisting for 15 to 20 sec.

(d) Calculation.—Calculate the percentage of copper as follows:

$$\text{Copper, per cent} = \frac{AB}{C} \times 100$$

where  $A$  = milliliters of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration of the sample,  
 $B$  = copper equivalent of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution, in grams per milliliter, and  
 $C$  = grams of sample used.

**2. Carbon Steels.**—Determine copper in accordance with the procedure described in Section 1, using 10 g. of the sample.

**3. Alloy Steels.**—Most alloy steels may be analyzed as described in Section 1, using 5 or 10 g. of the sample. When vanadium is present, it will be necessary to dis-

<sup>53</sup> Since molybdenum and vanadium interfere partly in this method, it is necessary, if the steel contains more than 0.25% of molybdenum or 0.05% of vanadium, to separate these elements from copper by treatment at this point with NaOH as described in Paragraphs (b) and (c) of the Gravimetric Method.

solve the precipitate of  $\text{CuS}$  (Section 1 (a)) and reprecipitate with  $\text{H}_2\text{S}$ , before proceeding in accordance with Section 1 (b).

4. *Tungsten Steels.*—(a) To 5 g. of the sample, add 75 ml. of  $\text{HCl}$  (1:1), and heat gently until the sample has dissolved. Carefully add 15 ml. of  $\text{HNO}_3$  (1:1) and boil gently until the tungstic acid becomes bright yellow. Dilute the solution to 100 ml. with boiling water, digest for several minutes, filter, and wash with  $\text{HCl}$  (1:9). For recovery of copper held by tungstic acid, see the section on procedure for copper in Tungsten Steels, Paragraph (c).

(b) Add 10 ml. of  $\text{H}_2\text{SO}_4$  to the filtrate and evaporate to dense white fumes. Cool, dilute to 200 ml., and heat to boiling. Add 20 ml. of  $\text{Na}_2\text{S}_2\text{O}_3$  (500 g. per liter), boil for 5 min., and complete the determination as described in Section 1.

5. *Cast Iron and High-Silicon Steels.*—(a) Dissolve 5 g. of the sample in 100 ml. of  $\text{H}_2\text{SO}_4$  (1:4). When solution is complete, evaporate to dense white fumes. Cool somewhat, dilute to 100 ml. with warm water, and heat until salts have dissolved. Filter, and wash the residue with hot water. Ignite in platinum at a temperature not exceeding  $550^\circ\text{C}$ . Add 2 ml. of  $\text{H}_2\text{SO}_4$  (1:1) and 3 to 5 ml. of  $\text{HF}$ , evaporate to dense white fumes, and cool. Add 10 ml. of water and filter into the main filtrate, washing the residue with hot water.

(b) Dilute the filtrate to 250 ml. and heat to boiling. Add 20 ml. of  $\text{Na}_2\text{S}_2\text{O}_3$  (500 g. per liter), continue the boiling for 5 min., and complete the determination as described in Section 1.

6. *Wrought Iron and Open-Hearth Iron.*—Determine copper in accordance with the procedure described in Section 1, using 10 g. of the sample.

### THE NEOCUPROINE (PHOTOMETRIC) METHOD (E30-60T)

*Scope and Application.*—This method covers the determination of copper in steels and cast irons in the range from 0.01 to 2.00%.

*Summary of Method.*—After solution in nitric acid, or nitric and hydrochloric acids, as the case may require, and fuming with perchloric acid, the salts are dissolved, and silver, if present, is removed with hydrochloric acid. Any insoluble matter is filtered off and the copper reduced in a citrate solution with hydroxylamine hydrochloride. The reduced copper is reacted with an ethanol solution of neocuproine, the complex extracted with chloroform, and the transmittance measured at 455  $\text{m}\mu$ .

*Concentration Range.*—The recommended concentration range is from 0.010 to 0.15 mg. of copper in 25 ml. of solution, using a cell depth of 1 cm. (Note 14).

NOTE 14.—This method has been written for a cell having a 1-cm. light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagent used.

*Stability of Color.*—The color is stable for at least 4 days.

*Interferences.*—Of the elements that can be present in steels and cast irons, only silver interferes directly. Provision is made in the method for its removal. Insoluble matter may be filtered off prior to color development. Traces of cyanide and sulfide interfere, but up to 5 ml. of phosphoric acid can be tolerated.

*Reagents.* (a) Chloroform.

(b) Copper, Standard Solution (1 ml. = 0.010 mg. Cu).—Transfer 0.1 g. of electrolytic copper, weighed to the nearest 0.1 mg., to a 250-ml. Erlenmeyer flask and add 10 ml. of  $\text{HNO}_3$  (1:1). Cover, and heat gently to effect solution. When the metal has dissolved, add 5 ml. of  $\text{HClO}_4$  and evaporate to fumes. Boil gently 5 min. and cool. Add 25 ml. of water, heat to boiling, and boil gently 2 min. and

evolve chlorine. Cool, transfer to a 1000-ml. volumetric flask, dilute to the mark, and mix. Transfer 100 ml. to a second 1000-ml. volumetric flask, dilute to the mark, and mix. This solution contains 0.010 mg. Cu per ml.

(c) **Hydroxylamine Hydrochloride Solution** (100 g. per liter).—Dissolve 10 g. of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) in 100 ml. of water.

(d) **Neocuproine Solution** (1 g. per liter).—Dissolve 0.1 g. of neocuproine (2,9-dimethyl-1,10-phenanthroline) in 100 ml. of ethanol (Note 15).

NOTE 15.—Some grades of denatured ethanol form unsuitable turbid solutions. Absolute methanol may be used, if desired.

(e) **Sodium Citrate Solution** (300 g. per liter).—Dissolve 300 g. of sodium citrate in 600 ml. of water and dilute to 1 liter.

**Preparation of Calibration Curve.** (a) **Calibration Solutions.**—By means of a 25-ml. buret, transfer 2, 4, 6, 8, 10, 12, and 15 ml. of copper solution (1 ml. = 0.010 mg. Cu) to seven 150-ml. beakers. To each beaker add 50 ml. of water, 10 ml. of the sodium citrate solution, and 5 ml. of the hydroxylamine hydrochloride solution. Stir well for 30 sec. (Note 16) and add 10 ml. of the neocuproine solution. Again stir and, using a pH meter, adjust the pH of the solution to about 5 with  $\text{NH}_4\text{OH}$  (1:1) (Note 17). Transfer the solution to a 250-ml. pear-shape separatory funnel, add 10 ml. of chloroform, and shake for 30 sec. After the aqueous and organic layers have separated, transfer the chloroform layer into a 25-ml. volumetric flask containing 4 ml. of ethanol. Make a second extraction with 5 ml. of chloroform and separate as before. Dilute to the mark with ethanol and mix.

NOTE 16.—Use of a magnetic stirrer is recommended for the stirring operation.

NOTE 17.—Since the reaction of copper with the reagent is complete within the pH range of 2.3 to 9.0, this adjustment can be made with pH paper; however, in highly-colored solutions use of a pH meter is preferable.

(b) **Reference Solution.**—Carry a reagent blank through all the steps of the procedure as directed in Paragraph (a).

(c) **Photometry.**—Transfer a portion of the reference solution to the absorption cell, and adjust the photometer to the initial setting, using a light band centered at approximately 455  $\mu$ . While maintaining this photometer adjustment, take the photometric readings of the calibration solutions.

(d) **Calibration Curve.**—Plot the photometric readings of the calibration solutions against milligrams of copper per 25 ml. of solution.

**Procedure.**—(a) Weigh to the nearest 1 mg. the amount of sample specified in Table 24-2, and transfer to a 250-ml. beaker. Add 15 ml. of  $\text{HNO}_3$  for plain carbon steels and cast irons, 10 ml. of  $\text{HNO}_3$  and 5 ml. of  $\text{HCl}$  for low-alloy steels and alloyed cast irons, and 10 ml. of  $\text{HCl}$  and 5 ml. of  $\text{HNO}_3$  for stainless steels. Cover and heat gently until the sample has dissolved.

(b) Wash cover and sides of beaker and add 1 ml. of  $\text{HF}$  (48%) for alloys containing more than 1.5% silicon, and add 0.5 ml. for those containing less. Add 15 ml. of  $\text{HClO}_4$  and evaporate to fumes; boil gently 5 min. and cool. Dissolve salts in 75 ml. of water.

(c) If any silver is present in the alloy, add 1 ml. of  $\text{HCl}$  at this point. Filter, if necessary, into a 200-ml. volumetric flask. Wash three times with 1%  $\text{HClO}_4$  and discard residue. Dilute to the mark and mix.

(d) By means of a pipet transfer the proper size aliquot (Table 24-2) to a 150-ml. beaker. Proceed as described in Paragraph (a), Preparation of Calibration Curve.

TABLE 24-2. SAMPLE SIZE AND DILUTION GUIDE

Copper, per cent	Sample Size, g.	Aliquot, ml.	Copper Content, mg.
0.01 to 0.15.....	1.0	20.0	0.01 to 0.150
0.10 to 0.25.....	1.0	10.0	0.05 to 0.125
0.20 to 0.50.....	0.5	10.0	0.05 to 0.125
0.40 to 1.00.....	0.5	5.0	0.05 to 0.125
0.80 to 2.00.....	0.25	5.0	0.05 to 0.125

(e) **Reference Solution.**—Add 50 ml. of water to a 150-ml. beaker and proceed as described in Paragraph (a) of Preparation of Calibration Curve.

(f) **Photometry.**—Take photometric readings of the sample solution as described in Paragraph (c) of Preparation of Calibration Curve.

**Calculation.**—Convert the photometric reading of the sample solution to milligrams of copper by means of the calibration curve. Calculate the percentage of copper as follows:

$$\text{Copper, per cent} = \frac{A}{B \times 10}$$

where  $A$  = milligrams of copper found in the aliquot used, and

$B$  = grams of sample represented in the aliquot used.

## NICKEL

### THE DIMETHYLGLYOXIME METHOD

**Reagents.** (a) **Tartaric Acid Solution** (250 g. per liter).—Dissolve 250 g. of tartaric acid in 600 ml. of water, filter, add 10 ml. of  $\text{HNO}_3$ , and dilute to 1 liter.

(b) **Alcohol Solution of Dimethylglyoxime** (10 g. per liter).

(c) **Tartaric Acid Solution** (20 g. per liter).—Dilute 80 ml. of tartaric acid (250 g. per liter) (Paragraph (a)) to 1 liter.

(d) **Potassium Thiocarbonate Solution.**—Saturate 125 ml. of KOH 50 g. per liter) with  $\text{H}_2\text{S}$ . Add 125 ml. of KOH (50 g. per liter) and 10 ml. of  $\text{CS}_2$  and heat moderately. Decant the dark red liquid from the undissolved  $\text{CS}_2$  and keep in a tightly closed flask.

(e) **Ethyl Ether.**

**Procedure.** 1. **Nickel Steels Containing 0.05 to 3.5% Nickel.**—(a) Transfer 1 g. of the sample <sup>54</sup> to a 400-ml. beaker, cover, and add 60 ml. of  $\text{HCl}$  (1:1).<sup>55</sup> Warm

<sup>54</sup> If the steel contains under 1% of nickel, 2- or 3-g. samples may be used with correspondingly larger amounts of tartaric acid. For steels containing more than 3.5% of nickel, either a sample equivalent to about 0.035 g. of nickel, or a suitable aliquot of a larger sample may be used.

<sup>55</sup> If the percentage of chromium is under 0.5%, the sample may be dissolved in 50 ml. of hot  $\text{HNO}_3$  (1:3).

until decomposition is complete, and then cautiously add 10 ml. of  $\text{HNO}_3$  (1:1). Boil until iron and carbides are oxidized and brown fumes have been expelled. Dilute to 200 ml. with hot water. Add 20 ml. of tartaric acid (250 g. per liter), neutralize with  $\text{NH}_4\text{OH}$ , and add 1 ml. of  $\text{NH}_4\text{OH}$  in excess. Filter, and wash the paper and residue with hot water containing a little  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{Cl}$ . Add  $\text{HCl}$  until slightly acid, warm to about  $60^\circ$  to  $80^\circ\text{C}$ ., and add 20 ml. of dimethylglyoxime solution (10 g. per liter). Add  $\text{NH}_4\text{OH}$  until slightly alkaline, and digest for 30 min. at about  $60^\circ\text{C}$ . Cool to room temperature.<sup>56</sup>

(b) Complete the determination by the gravimetric method (Paragraphs (c) to (f)) or the electrolytic method (Paragraphs (g) to (i)).

**Gravimetric Method.**—(c) Filter through a weighed Gooch crucible under light suction, but do not allow the mat to run dry; wash the precipitate thoroughly with cold water. Fritted-glass or other porous crucibles may also be used. If fritted-glass crucibles are used, it is advisable to allow a thin mat of the precipitate to form before strong suction is applied. Add 5 ml. of dimethylglyoxime (10 g. per liter) and 0.5 ml. of  $\text{NH}_4\text{OH}$  to the filtrate and washings. Stir, and allow to stand to determine whether precipitation is complete.

(d) If appreciable cobalt (over 1%) or copper (over 4%) is present, add sufficient dimethylglyoxime to take care of them as well as the nickel, and preferably reprecipitate the nickel as follows: when the precipitate has been washed, discontinue the suction, place the original beaker under the funnel, and add a hot mixture of 20 ml. of  $\text{HCl}$  (1:1) and 5 ml. of  $\text{HNO}_3$ . After 1 min., apply suction until dry, repeat the treatment with 25 ml. of the  $\text{HCl-HNO}_3$  mixture, drain, and wash thoroughly with 50 ml. of hot tartaric acid (20 g. per liter). Nearly neutralize the absolutely clear solution with  $\text{NH}_4\text{OH}$  and precipitate with dimethylglyoxime and  $\text{NH}_4\text{OH}$  as before. A dimethylglyoxime precipitate contaminated by cobalt is a darker red than a pure nickel dimethylglyoxime.

(e) Dry the precipitate (Paragraph (c) or (d)) at  $150^\circ\text{C}$ . to constant weight. Cool in a desiccator and weigh as nickel dimethylglyoxime.

(f) **Calculation.**—Calculate the percentage of nickel as follows:

$$\text{Nickel, per cent} = \frac{A \times 0.2032}{B} \times 100$$

where  $A$  = grams of nickel dimethylglyoxime, and

$B$  = grams of sample used.

**Electrolytic Method.**—(g) Filter the nickel dimethylglyoxime precipitate (Paragraph (a)) on a 12- or 15-cm. paper and wash thoroughly 18 to 20 times with hot water.

(h) Dissolve the precipitate in hot  $\text{HNO}_3$  (1:3) and wash the filter thoroughly with hot water. Add 20 ml. of  $\text{H}_2\text{SO}_4$  (1:1) and evaporate to dense white fumes. Cool somewhat, add 10 ml. of  $\text{HNO}_3$ , and repeat the evaporation to dense white fumes. Rinse the cover and sides of the beaker with water and heat the solution to white fumes again to insure the expulsion of every trace of the  $\text{HNO}_3$ . Cool, add 50 ml. of cold water, and heat until salts are dissolved.

(i) Neutralize with  $\text{NH}_4\text{OH}$  and add an excess of 25 ml. of  $\text{NH}_4\text{OH}$ . Dilute to 175 ml. and electrolyze at a current density of from 1 to 2 amp. per sq. dm. Con-

<sup>56</sup> If the amount of nickel is small (under 0.2%), or if much cobalt is present, the solution should be allowed to stand at room temperature overnight and filtered cold.

tinue the electrolysis until the solution has become colorless (5 to 8 hr.). The solution may be tested for complete electrolysis by adding one or two drops of it to 1 ml. of potassium thiocarbonate solution. A pink or red color indicates the presence of nickel.

(j) When deposition of the nickel is complete, lower the electrolytic beaker quickly, with the current still on, while rinsing the cathode with water from a wash bottle. Turn off the current, quickly detach the cathode and rinse it in a beaker of water, and then dip it in two successive baths of ethanol or methanol. Dry in an oven at 110°C. for 3 to 5 min., cool (preferably in a desiccator), and weigh the deposit as metallic nickel.

(k) In very accurate work, dissolve the deposit in warm  $\text{HNO}_3$ , wash the cathode with water, then alcohol, dry for a few minutes at 110°C., and reweigh.

(l) **Calculation.**—Calculate the percentage of nickel as follows:

$$\text{Nickel, per cent} = \frac{A}{B} \times 100$$

where  $A$  = grams of nickel, and

$B$  = grams of sample used.

**2. High-Chromium, High-Nickel Steels (20% Chromium, 20% Nickel; 18% Chromium, 8% Nickel; etc.).**—Transfer 0.35 to 0.5 g.<sup>57</sup> of the sample to a 400-ml. beaker, and add 20 ml. of  $\text{HCl}$  (1:1) and 20 ml. of  $\text{HNO}_3$  (1:1). Heat until solution is complete, add 20 ml. of  $\text{HClO}_4$ , and evaporate to fumes (for low-carbon, low-silicon alloys this latter step may be omitted). Cool somewhat, and add 100 ml. of water. Warm until salts dissolve, filter, and complete the determination as described in Section 1, adding sufficient dimethylglyoxime (10 g. per liter) to precipitate all of the nickel (20 to 40 ml.).

**3. Carbon Steels and Other Steels Containing Under 0.05% Nickel.**—(a) Transfer 5 g. of the sample to a 400-ml. beaker and add 40 ml. of  $\text{HCl}$  (1:1). Heat until solution is complete, and then carefully add 15 ml. of  $\text{HNO}_3$  (1:1). Evaporate to a volume of about 15 ml. and add 50 ml. of  $\text{HCl}$  (1:1).

(b) Transfer to a 200-ml. separatory funnel, rinsing the beaker with several 15-ml. portions of  $\text{HCl}$  (1:1). Cool to 10°C., add 120 ml. of ethyl ether, and carefully shake for 1 to 2 min. in a stream of cold water. Let settle for several minutes and then draw off the lower clear solution into the original beaker.

(c) Gently heat the solution in the beaker to expel the ether (avoid free flames). Add 0.3 g. of  $\text{KClO}_3$ , boil until the  $\text{KClO}_3$  is decomposed, dilute to 100 ml., and add 3 g. of tartaric acid. Make the solution alkaline with  $\text{NH}_4\text{OH}$  and filter. Acidify with  $\text{HCl}$  and complete the determination as described in Section 1.

**4. Cast Iron and High-Silicon Steels.**—(a) Dissolve 5 g. of the sample in 40 ml. of  $\text{HCl}$  (1:1), carefully add about 15 ml. of  $\text{HNO}_3$  (1:1) to oxidize the iron, and evaporate to dryness. Drench the hot, dried mass with 10 ml. of  $\text{HCl}$  and then dilute with 75 ml. of hot water. Filter, wash with  $\text{HCl}$  (1:1), and evaporate the filtrate to a sirupy consistency.

(b) Add 50 ml. of  $\text{HCl}$  (1:1), transfer to a 200-ml. separatory funnel, rinse the beaker with several small portions of  $\text{HCl}$  (1:1), add 120 ml. of ethyl ether, and complete the determination as described in Section 3.

<sup>57</sup> If the percentage of chromium is under 0.5%, the sample may be dissolved in 50 ml. of hot  $\text{HNO}_3$  (1:3).

5. *High-Nickel, Chromium Alloy Cast Iron (15% Nickel, 6% Copper, 2% Chromium; etc.).*—(a) Transfer 2.5 g. of the sample to a 400-ml. beaker or flask and add a mixture of 25 ml. of HCl and 25 ml. of HNO<sub>3</sub>. When solution is complete, add 30 ml. of HClO<sub>4</sub> and 5 to 10 drops of HF, and fume for 10 to 15 min. after the chromium has been oxidized. Cool somewhat, add 100 ml. of water, and heat to boiling. Filter and wash well with HCl (5:95), catching the filtrate and washings in a 250-ml. volumetric flask.<sup>58</sup> Mix the contents, cool to room temperature, dilute to the mark, and mix thoroughly.

(b) Pipet 50-ml. aliquots and proceed by the dimethylglyoxime-electrolytic method as described in Section 1 (a), (b), and (g) to (l). Either dissolve and reprecipitate the nickel dimethylglyoxime (Section 1 (d)), or determine any occluded copper in the deposit and correct the results accordingly.

6. *Open-Hearth Iron and Wrought Iron.*—Determine nickel in accordance with the procedure described in Section 3.

7. *Nickel Wrought Iron.*—Determine nickel in accordance with the procedure described in Section 1. Dissolve the first dimethylglyoxime precipitate and again precipitate nickel with dimethylglyoxime as directed in Section 1 (d).

## THE CYANIDE TITRATION METHOD

*Reagents.* (a) Sulfuric-Citric Acid Mixture.—Dissolve 200 g. of citric acid in 1 liter of cool H<sub>2</sub>SO<sub>4</sub> (1:9).

(b) Standard Silver Nitrate Solution (1 ml. = 0.001 g. Ni).

(c) Potassium Iodide Solution (100 g. per liter).

(d) Standard Potassium Cyanide Solution (1 ml. = 0.001 g. Ni).—Dissolve 4.5 g. of KCN in 1 liter of water containing 1 g. of KOH and standardize against the standard AgNO<sub>3</sub> solution. The KCN solution changes with age, so it must be standardized frequently.

(e) Ethyl Ether.

(f) Hydrogen Sulfide Wash Solution.—Saturate HCl (1:99) with H<sub>2</sub>S.

*Procedure.* 1. *Nickel Steels.*

(1) Titration Following a Preliminary Precipitation with Dimethylglyoxime.<sup>59</sup>

—(a) Precipitate the nickel in 1 g. of the sample as described in Section 1 (a). Dissolve the washed precipitate with a hot mixture of 20 ml. of HCl (1:1) and 5 ml. of HNO<sub>3</sub> in a 400-ml. beaker.<sup>60</sup> Evaporate the solution to 50 ml. or until free of dimethylglyoxime and oxidizing gases. Cool the solution and add 10 ml. of sulfuric-citric acid mixture. Make nearly alkaline with NH<sub>4</sub>OH, again cool, dilute to 200 ml., and complete the neutralization as follows: add exactly 2 ml. of AgNO<sub>3</sub> (1 ml. = 0.001 g. Ni) and, if no precipitate appears, add HCl (1:10) until a precipitate of AgCl forms. Then add NH<sub>4</sub>OH (1:1) drop by drop, while stirring constantly, until the precipitate just dissolves. Add 3 ml. of NH<sub>4</sub>OH and 2 ml. of KI (100 g. per liter) and titrate with KCN (1 ml. = 0.001 g. Ni), while stirring constantly, until the solution becomes perfectly clear.

(b) Determine the volume of KCN solution equivalent to exactly 2 ml. of the AgNO<sub>3</sub> solution.

<sup>58</sup> The residue sometimes contains appreciable amounts of nickel. This may be recovered by igniting, treating with HF, evaporating, fusing the residue with a small amount of K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, dissolving, and adding to the main solution.

<sup>59</sup> This method may be applied to steels containing cobalt, copper, and tungsten.

<sup>60</sup> If the steel contains more than 4% of copper or 2% of cobalt, the nickel should be reprecipitated with dimethylglyoxime as described in Section 1 (d).

(c) **Calculation.**—Calculate the percentage of nickel as follows:

$$\text{Nickel, per cent} = \frac{(A - B)C}{D} \times 100$$

where  $A$  = milliliters of KCN solution required for titration of the sample,  
 $B$  = milliliters of KCN solution equivalent to the  $\text{AgNO}_3$  solution added,  
 $C$  = nickel equivalent of the KCN solution, in grams per milliliter, and  
 $D$  = grams of a sample used.

(2) **Titration Following a Preliminary Extraction with Ether.**<sup>61</sup>—(a) Transfer 1 g. of the sample to a 150-ml. beaker, cover, and add 20 ml. of  $\text{HCl}$  (5:2). When reaction ceases, carefully add 4 ml. of  $\text{HNO}_3$  (5:2), and boil until brown fumes have been expelled.

(b) Cool, transfer the solution to a 200-ml. separatory funnel, and rinse the beaker with  $\text{HCl}$  (5:2). Cool to  $10^\circ\text{C}$ ., add 40 ml. of ethyl ether (perform this operation away from open flames or hot plates), and shake gently for a few minutes. Let settle for 2 min., and draw off the acid layer into a 250-ml. beaker. Add 5 ml. of  $\text{HCl}$  (5:2) to the ether portion. Cool, shake, let settle for 1 min., draw off the acid layer, and add it to the main extract.

(c) Heat gently to expel dissolved ether, add 0.2 g. of  $\text{KClO}_3$ , and boil until the chlorine is driven off. Dilute to 100 ml. with water, neutralize with  $\text{NH}_4\text{OH}$ , add an excess of 3 to 4 ml., and boil for a few minutes. Filter and wash with hot water. Add 10 ml. of  $\text{HCl}$  to the filtrate, heat just short of boiling, and pass  $\text{H}_2\text{S}$  into the solution. Filter and wash with  $\text{H}_2\text{S}$  wash solution.

(d) Boil to expel  $\text{H}_2\text{S}$ . Cool, dilute to 200 ml., add 10 ml. of the sulfuric-citric acid mixture, and complete the determination as described in Section (1).

## THE DIMETHYLGLYOXIME (PHOTOMETRIC) METHOD (E30-60T) (FOR ALLOYS CONTAINING NOT MORE THAN 4% NICKEL)

**Summary of Method.**—Nickelous ions, oxidized by means of iodine, react with dimethylglyoxime in an ammoniacal medium to form the soluble colored compound, nickel dimethylglyoxime.

**Concentration Range.**—The concentration range should not exceed 0.3 mg. of nickel in 50 ml. of solution, using a cell depth of 1 cm. (Note 17A).

**NOTE 17A.**—This procedure has been written for cells having 1-cm. and 2-cm. light paths and a "narrow-band" instrument. The concentration range depends upon band width and spectral region used as well as cell depth; calibration data should cover the range of 20 to at least 70% transmittance.

**Stability of Color.**—In the absence of manganese, copper, and cobalt, the color develops fully within 1 or 2 min., and it is stable for 20 to 30 min.

**Interfering Elements.**—(a) Copper, manganese, and cobalt interfere by forming colored compounds with dimethylglyoxime. The method provides for the derivation of correction factors (Note 18) which permit the accurate determination of nickel in the presence of limited amounts of these elements.

**NOTE 18.**—In many types of alloys the interfering elements are too low to be significant as indicated by the following nominal values for the correction factors:  $F(\text{Cu})$  and  $F(\text{Mn})$ , 0.004 to 0.007;  $F(\text{Co})$ , 0.002 to 0.004. The corrections may be ignored, or a nominal cor-

<sup>61</sup> This method is not applicable to steels containing cobalt or more than 1% of tungsten.



rection may be made in lieu of the following sections on evaluation of copper, manganese, and cobalt interference, depending upon the nature of the sample and the accuracy required.

(b) Copper induces fading of the nickel dimethylglyoxime, which is not serious until 10 min. has elapsed after adding dimethylglyoxime. However, if the ratio of copper to nickel is above a critical level (see Table 24-3), fading precludes the possibility of accurate measurement of the absorbance, and the correction factor is not valid. In extreme cases, copper must be removed prior to the determination of nickel.

(c) The rate of fading due to the presence of copper increases with temperature above 25°C. This requires that two correction factors be determined, one to apply at temperatures below 25°C., and the other to apply within the range of 25° to 30°C. The method cannot be applied at higher temperatures unless the copper content of the solution is less than 0.1 mg.

TABLE 24-3. SAMPLE SIZE AND DILUTION GUIDE

Ni, per cent	Sample, g. per 200 ml.	Aliquot, ml. <sup>a</sup>	Nickel Added to Aliquot, mg.	Celi Length, cm.
0.01 to 0.15..... (Mn, 3% max.; Cu, 1% max.)	0.500	20	0.08	2
0.01 to 0.15 . . . (Mn, 4% max.; Cu, 1.3% max.)	0.500	15	0.08	2
0.15 to 0.65..... (Mn, 4% max.; Cu, 1.3% max.)	0.500	15	0	1
0.35 to 1.10.....	0.500	10	0	1
0.70 to 2.10.....	0.240	10	0	1
1.90 to 4.15.... (Mn, 4% max.; Cu, 2.0% max.)	0.120	10	0	1

<sup>a</sup> Co not to exceed 2 mg.

(d) Manganese may retard the color development noticeably if the ratio of manganese to nickel is high; above the critical level of this ratio (see Table 24-3) it is necessary to add nickel to the sample solution to induce color development to take place within the 10-min. time interval.

(e) Cobalt reacts with dimethylglyoxime, thus limiting the amount of nickel that may react with a given amount of the reagent. If cobalt is high, it is necessary to limit the amount of cobalt to 2.0 mg. in the aliquot used for the nickel determination. At this absolute level of cobalt not more than 0.15 mg. of nickel may be present without rendering the correction factor invalid.

(f) The high-absorbance region of ferric citrate is avoided by measuring the absorbance of nickel dimethylglyoxime at 540  $m\mu$ .

**Apparatus.** Volumetric Flasks.—These should be of borosilicate glass, glass-stoppered, 200-ml. capacity.

**Reagents.** (a) Ammonium Citrate Solution (540 g. per liter).—Dissolve 540 g. of ammonium citrate in water and dilute to 1 liter. Filter the solution, if necessary.

(b) Dimethylglyoxime Solution.—Dissolve 1.0 g. of dimethylglyoxime in 500 ml. of  $NH_4OH$  and dilute to 1 liter.

(c) Iodine Solution (0.02 N).—Dissolve 8 g. of KI and 2.6 g. of iodine in a minimum of water and dilute to 1 liter.

(d) Standard Nickel Solution (1 ml. = 0.4 mg. Ni).—Dissolve 0.4000 g. of high-purity nickel (containing not less than 99.7% Ni, and less than 0.1% each of Cu, Mn, and Co) in 15 ml. of hot  $HNO_3$  (1:1). Add 15 ml. of  $HClO_4$  and evaporate to fumes. Cool, add 50 ml. of water, and digest until the salts are dissolved. Cool, dilute to 1 liter, and mix.

(e) Standard Nickel Solution (1 ml. = 0.01 mg. Ni).—Transfer 25.00 ml. of the nickel solution (1 ml. = 0.4 mg. Ni) to a 1-liter volumetric flask, add 5 ml. of  $HClO_4$ , dilute to volume, and mix.

(f) Standard Nickel Solution (1 ml. = 0.016 mg. Ni).—Transfer 20.00 ml. of the nickel solution (1 ml. = 0.4 mg. Ni) to a 500-ml. volumetric flask. Add 5 ml. of  $HClO_4$ , dilute to volume, and mix.

(g) Standard Nickel Solution (1 ml. = 0.0060 mg. Ni).—Transfer 15.00 ml. of the nickel solution (1 ml. = 0.4 mg. Ni) to a 1-liter volumetric flask, add 5 ml. of  $HClO_4$ , dilute to volume, and mix.

(h) Standard Iron Solution (1 ml. = 5.0 mg. Fe).—Dissolve 2.50 g. of high-purity iron (containing less than 0.1% each of Ni, Cu, Mn, and Co) in 25 ml. of  $HCl$  (1:1) and add 3 to 4 ml. of  $HNO_3$  and 30 ml. of  $HClO_4$ . Heat to fumes, cool, dilute to 500 ml., and mix.

(i) Standard Copper Solution (1 ml. = 0.1 mg. Cu).—Dissolve 0.100 g. of high-purity copper (containing less than 0.1% each of Ni, Mn, and Co) in 10 ml. of  $HNO_3$ , add 50 ml. of water, and boil for 5 min. Cool, dilute to 1 liter, and mix.

(j) Standard Manganese Solution (1 ml. = 0.1 mg. Mn).—Dissolve 0.100 g. of high-purity manganese (containing less than 0.1% each of Ni, Cu, and Co) in 10 ml. of  $HNO_3$ , add 50 ml. of water, and boil for 5 min. Cool, dilute to 1 liter, and mix.

(k) Standard Cobalt Solution (1 ml. = 0.4 mg. Co).—Dissolve 0.200 g. of high-purity cobalt (containing less than 0.1% each of Ni, Cu, and Mn) in 15 ml. of  $HNO_3$ , add 50 ml. of water, and boil for 5 min. Cool, dilute to 500 ml., and mix.

**Preparation of Calibration Curve.**—(a) By means of pipets, transfer 5, 10, 15, 20, and 25 ml. of nickel solution (1 ml. = 0.01 mg. Ni for 1-cm. cells and 1 ml. = 0.0060 mg. Ni for 2-cm. cells) to 50-ml. volumetric flasks. Add 5.0 ml. of ammonium citrate solution to each flask and mix. Add 5 ml. of iodine solution to each flask and mix. (Prepare a duplicate at each level of nickel.)

(b) At each nickel level add 10 ml. of  $NH_4OH$  (1:1) to one set to be used as a

reference solution, and 10 ml. of dimethylglyoxime solution to the other set, agitating during the addition. Dilute each solution to volume, stopper the flask, and mix.

(c) Measure the transmittance of the test solution, 10 min. after adding the dimethylglyoxime, against the reference solution, at 540  $m\mu$ . Convert the transmittance to absorbance,  $A = \log 1/T$ .

(d) Transfer 15 ml. of water and 0.5 ml. of  $\text{HClO}_4$  to each of two 50-ml. volumetric flasks; prepare one solution as a reference solution and the other as a test solution and proceed according to Paragraph (a), and then add  $\text{NH}_4\text{OH}$  (1:1) and dimethylglyoxime solution in accordance with Paragraph (b). Record the absorbance as the reagent blank.

(e) Fill the two cells with a reference solution and measure the transmittance at 540  $m\mu$ , convert to absorbance, and record as the cell correction.

(f) Apply the cell correction to the absorbance values obtained in Paragraphs (c) and (d). Subtract the corrected absorbance for the reagent blank from the corrected gross absorbance (Paragraph (c)).

(g) Calculate the ratio, mg. Ni/ $A$ , at each level of nickel. If the ratios are constant, within experimental error, calculate the average value of the ratios to find the factor to apply to convert absorbance to milligrams of nickel. If the ratios are not constant, or if for other reasons it is desirable, plot the values obtained against milligrams of nickel per 50 ml. of solution.

**Evaluation of Copper Interference (Note 18).**—(a) Transfer 5.00 ml. of nickel solution (1 ml. = 0.016 mg. Ni) and 10.0 ml. of iron solution (1 ml. = 5.0 mg. Fe) to each of four 50-ml. volumetric flasks. Transfer 5.0 ml. of copper solution (1 ml. = 0.1 mg. Cu) to each of two of the flasks.

(b) Add 5.0 ml. of ammonium citrate solution and 5 ml. of iodine solution to each flask. Treat the two solutions containing nickel, and, in turn, the two solutions containing nickel plus copper, in accordance with the section on preparation of calibration curve, (b) and (c), using 2-cm. cells.

(c) Subtract the absorbance value obtained for nickel from that found for nickel plus copper and calculate the copper correction factor as follows:

$$F(\text{Cu}) = F \times \frac{A(\text{Cu})}{0.5}$$

where  $F$  = factor, mg. Ni/ $A$  (2-cm. cells), and

$A(\text{Cu})$  = absorbance due to 0.5 mg. of copper.

**Evaluation of Manganese Interference (Note 18).**—Transfer 5.00 ml. of nickel solution (1 ml. = 0.016 mg. Ni) and 10.0 ml. of iron solution (1 ml. = 5.0 mg. Fe) to each of four 50-ml. volumetric flasks. Transfer 5.0 ml. of manganese solution (1 ml. = 0.1 mg. Mn) to each of two of the flasks. Proceed in accordance with the section on evaluation of copper interference, (b) and (c), with manganese substituted for copper, to determine the manganese correction factor,  $F(\text{Mn})$ .

**Evaluation of Cobalt Interference (Note 18).**—(a) Transfer 5.00 ml. of nickel solution (1 ml. = 0.016 mg. Ni) and 10.0 ml. of iron solution (1 ml. = 5.0 mg. Fe) to each of four 50-ml. volumetric flasks. Transfer 5.0 ml. of cobalt solution (1 ml. = 0.4 mg. Co) to each of two of the flasks. Proceed in accordance with the section on evaluation of copper interference, (b).

(b) Subtract the absorbance value obtained for nickel from that found for nickel plus cobalt and calculate the cobalt correction factor as follows:

$$F(\text{Co}) = F \times \frac{A(\text{Co})}{2.0}$$

where  $F$  = factor, mg. Ni/ $A$  (2-cm. cells), and  
 $A(\text{Co})$  = absorbance due to 2.0 mg. of cobalt.

**Procedure.**—(a) Transfer the sample (Table 24-3) to a 200-ml. borosilicate glass volumetric flask, add 8 to 10 ml. of  $\text{HCl}$  (1:1), and heat until the sample is decomposed. Add 3 to 4 ml. of  $\text{HNO}_3$ , and 10 ml. of  $\text{HClO}_4$ . If the silicon content of the sample is more than 1%, add 2 to 3 ml. of  $\text{HF}$  before adding the  $\text{HClO}_4$ .

(b) Fume to expel  $\text{HCl}$  and  $\text{HNO}_3$  and, if tungsten is present, fume until the tungstic acid is bright yellow. Cool, add 50 ml. of water, and digest to dissolve the salts.

(c) Cool, dilute to volume, and mix. Allow insoluble matter to settle, or dry-filter before taking aliquots (Note 19).

NOTE 19.—Deposits of silicic acid or tungstic acid that cling to the walls of the flask can be removed by means of  $\text{NH}_4\text{OH}$ ; it may, however, be desirable to dissolve the samples and fume with  $\text{HClO}_4$  in an Erlenmeyer flask or a covered beaker.

(d) Transfer identical aliquots (Table 24-3) to each of two 50-ml. volumetric flasks. If necessary (see Table 24-3), add 5.00 ml. of the nickel solution (1 ml. = 0.016 mg. Ni). Add 5.0 ml. of ammonium citrate solution and 5 ml. of iodine solution to each solution. Proceed in accordance with the section on preparation of calibration curve, (b), (c), and (f).

(e) Calculate the percentage of nickel as follows:

$$\text{Nickel, per cent} = \frac{[(A \times F) - B]V_1 \times 100}{V_2 \times W} - \text{Cu, per cent} \times F(\text{Cu}) - \text{Mn, per cent} \times F(\text{Mn}) - \text{Co, per cent} \times F(\text{Co})$$

where

$A$  = corrected absorbance,

$F$  = factor, mg. Ni/ $A$ ,

$B$  = nickel added, in milligrams,

$V_1$  = dilution of sample solution, in milliliters,

$V_2$  = aliquot of sample solution, in milliliters,

$W$  = sample weight, in milligrams,

Cu, per cent = copper in the sample, in per cent,

$F(\text{Cu})$  = copper correction factor,

Mn, per cent = manganese in the sample, in per cent,

$F(\text{Mn})$  = manganese correction factor,

Co, per cent = cobalt in the sample, in per cent, and

$F(\text{Co})$  = cobalt correction factor.

## CHROMIUM

### THE PERSULFATE OXIDATION METHOD

**Reagents.** (a) Sulfuric-Phosphoric Acid Mixture.—Add slowly, while stirring, 320 ml. of  $\text{H}_2\text{SO}_4$  (1:1) to 600 ml. of water. Cool, and add 80 ml. of  $\text{H}_3\text{PO}_4$ .

(b) Silver Nitrate Solution (10 g. per liter).

(c) Ammonium Persulfate Solution (150 g. per liter).—Prepare fresh as required.

(d) Standard Ferrous Ammonium Sulfate Solution (0.08 N).—To obtain the ratio

of the ferrous ammonium sulfate solution to the  $\text{KMnO}_4$  solution (Paragraph (c)), take 25 ml. of the ferrous ammonium sulfate solution, dilute to 350 ml. with cool  $\text{H}_2\text{SO}_4$  (5:95), add 2 ml. of  $\text{H}_3\text{PO}_4$ , and titrate with the  $\text{KMnO}_4$  to a faint persistent pink tint. Determine the blank on the same volume of water and acids, deduct, and calculate the volume of  $\text{KMnO}_4$  that is equivalent to 1 ml. of the ferrous ammonium sulfate solution. The ratio of the ferrous ammonium sulfate solution to the  $\text{KMnO}_4$  must be determined daily unless the ferrous solution is kept under hydrogen. Stronger solutions of ferrous ammonium sulfate and  $\text{KMnO}_4$  may, of course, be prepared for use with high-chromium steels. Approximately 0.1 *N* solutions are desirable with material containing over 3% chromium.

(e) Standard Potassium Permanganate Solution (0.06 *N*).

**Procedure. 1. Chromium Steels.**—(a) Transfer 2 g. of the sample, for steels containing less than 2% chromium, to a 600-ml. beaker and add 60 ml. of the  $\text{H}_2\text{SO}_4$ - $\text{H}_3\text{PO}_4$  mixture. Heat until action ceases, cautiously add 10 ml. of  $\text{HNO}_3$  (1:1), and boil until all carbides are dissolved and brown fumes have been expelled. With steels containing between 2 and 5% chromium, dissolve 1 g. of the sample, evaporate until salts separate, dilute with about 50 ml. of warm water, add 5 to 10 ml. of  $\text{HNO}_3$ , and again carefully evaporate until salts separate. If carbides still persist, filter, wash the paper with warm water, ignite the paper and residue, fuse with  $\text{Na}_2\text{CO}_3$ , and add the solution of the melt to the main solution.

(b) After the sample is completely dissolved, dilute to 300 ml. with hot water and add 5 ml. of  $\text{AgNO}_3$  (10 g. per liter) and 20 ml. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (150 g. per liter). Boil the solution for 8 to 10 min. If the color of permanganic acid does not develop, add more  $\text{AgNO}_3$  and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , and again boil for 10 min. Add 5 ml. of  $\text{HCl}$  (1:3) and continue the boiling for 5 min. after the pink color has just disappeared. If the permanganic acid color is not destroyed by boiling for 10 min., or if a precipitate of  $\text{MnO}_2$  remains, add 2 to 3 ml. more of  $\text{HCl}$  (1:3) and boil as before. The total period of boiling after the addition of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  shall be not less than 15 min., 30 min. will do no harm, provided the volume is maintained at approximately 300 ml. by the addition of hot water at intervals.

(c) Cool the solution, dilute to 400 ml., and add a measured volume of 0.08 *N* ferrous ammonium sulfate (25 ml. for steel containing under 1.5% chromium, 50 ml. for 1.5 to 3% chromium, etc.). Stir and titrate with the 0.06 *N*  $\text{KMnO}_4$ <sup>62</sup> until an end point is obtained that persists, upon continued stirring, for 1 min.<sup>63</sup>

(d) The titration must be corrected for dilution effect and color interference. The correction may be made: (1) empirically; <sup>64</sup> (2) by titrating the same volume of

<sup>62</sup> In the absence of tungsten, the end point may be obtained by potentiometric titration with standard ferrous ammonium sulfate solution. In this case, the ferrous solution is standardized with recrystallized  $\text{K}_2\text{Cr}_2\text{O}_7$ . Vanadium is included in this titration. If present, it must be determined and subtracted from the apparent chromium value (vanadium, per cent  $\times 0.34$  = chromium, per cent). With tungsten steels the potentiometric procedure is modified by omitting  $\text{H}_3\text{PO}_4$  and oxidizing tungsten to tungstic acid with  $\text{HNO}_3$  (when  $\text{H}_3\text{PO}_4$  is added to hold tungsten in solution the potentiometric end point with  $\text{FeSO}_4$  is difficult to detect).

<sup>63</sup> In the absence of vanadium the first end point is permanent, but if vanadium is present, the end point will fade at first, owing to the slow oxidation of vanadium from the quadrivalent to the quinquevalent stage in a cold solution.

<sup>64</sup> In this correction the dilution effect is ignored and the volume of  $\text{KMnO}_4$  used in overcoming the green color is taken as equivalent to 0.6% of the chromium present. The correction is usually applied to the chromium equivalent of the solution, as, for example, by using the equivalent 0.01744 g. instead of 0.01734 g. of chromium per milliliter of 1 *N* ferrous ammonium sulfate solution.

0.08 *N* ferrous ammonium sulfate in a solution of like volume and acidity, and containing the same amounts of the coloring elements in their final valencies; or (3) by a second titration of the final solution. The last method is the most convenient and satisfactory in occasional analyses, and may be performed by boiling the solution that has just been titrated for 10 min. in order to destroy the slight excess of permanganate, cooling to room temperature, and then titrating with 0.06 *N*  $\text{KMnO}_4$  to the color that was originally taken as the end point. The titrated solution may be reserved for the determination of vanadium.

(e) **Calculation.**—Calculate the percentage of chromium as follows:

$$\text{Chromium, per cent} = \frac{[AB - (C - D)]E \times 0.01734}{F} \times 100$$

where *A* = milliliters of ferrous ammonium sulfate solution added (Paragraph (c)),

*B* = milliliters of  $\text{KMnO}_4$  solution equivalent to 1 ml. of the ferrous ammonium sulfate solution,

*C* = milliliters of  $\text{KMnO}_4$  solution required for titration (Paragraph (c)),

*D* = milliliters of  $\text{KMnO}_4$  solution required for the end point correction (Paragraph (d)),

*E* = normality of the  $\text{KMnO}_4$  solution, and

*F* = grams of sample used.

**2. High-Chromium, High-Nickel Steels.**—(a) Transfer 0.5 g. of the sample to a 600-ml. beaker and add 75 ml. of  $\text{H}_2\text{SO}_4$  (1:4). When solution is complete, evaporate until salts just separate, cool, dilute to 70 ml., and dissolve the iron salts. Oxidize the iron by the cautious addition of  $\text{HNO}_3$ . Add 3 to 4 drops of HF and again evaporate to incipient fumes of  $\text{H}_2\text{SO}_4$ . Cool, dilute to 300 ml. with hot water, add 10 ml. of  $\text{AgNO}_3$  (10 g. per liter) and 15 g. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , and boil the solution for 10 to 12 min. Add 5 ml. of HCl (1:3) and complete the determination as described in Section 1 above. Stronger solutions of ferrous ammonium sulfate and  $\text{KMnO}_4$  are more convenient for use with high-chromium steels.

(b) The visual end point in high-chromium steels can be detected more easily when oxidation-reduction indicators are used, that is, 1,10-phenanthroline ferrous complex for the ferrous ammonium sulfate-potassium permanganate titration (Section 1) or diphenylamine sulfonic acid with a ferrous ammonium sulfate-potassium dichromate titration. With 1,10-phenanthroline (1 to 2 drops of the 0.025 *M* indicator) the end point in the ferrous ammonium sulfate-potassium permanganate titration is indicated by the change in color from pink to clear green (persisting for 60 sec.). With diphenylamine sulfonic acid, the chromic acid is titrated with the ferrous ammonium sulfate solution to a clear green end point. The ferrous ammonium sulfate solution in this case is standardized against either a standard chromium steel or pure  $\text{K}_2\text{Cr}_2\text{O}_7$ . Vanadium, if present, will also be titrated with both indicators as in the potentiometric method. When 1,10-phenanthroline is used, the vanadium may be determined in the same solution, after the initial end point is obtained, by reducing the acidity of the solution with 23 g. of sodium acetate and titrating slowly at 50°C. with 0.06 *N*  $\text{KMnO}_4$  to the green end point.

**3. Cast Iron Containing Over 0.15% Chromium.**—(a) Transfer 2 g. of the sample to a 600-ml. beaker and add 60 ml. of the  $\text{H}_2\text{SO}_4$ - $\text{H}_3\text{PO}_4$  mixture. Heat until action ceases, add 15 ml. of  $\text{HNO}_3$  (1:1), and boil until brown fumes have been expelled. Evaporate until salts separate, dilute with about 50 ml. of warm water, and digest until salts are dissolved. Filter and wash the paper with warm water. If

chromium is less than 0.75%, the residue will be practically free of chromium. To recover any insoluble chromium, ignite the paper and insoluble matter until all carbon is consumed.

(b) Treat the residue with HF and  $\text{H}_2\text{SO}_4$ , fuse with  $\text{Na}_2\text{CO}_3$ , and add the solution of the melt to the main solution. To the combined solutions add 5 ml. of  $\text{AgNO}_3$  (10 g. per liter), dilute to 300 ml. with boiling water, and complete the determination as described in Section 1.

4. *High-Nickel Chromium Alloy Cast Iron (15% Nickel, 6% Copper, 2% Chromium; etc.)*. Transfer 2 g. of the sample to a 500-ml. Erlenmeyer flask and add 20 ml. of a mixture of equal parts of HCl and  $\text{HNO}_3$ . Heat until action ceases. Then add 15 ml. of  $\text{HClO}_4$  and 5 drops of HF, and evaporate to white fumes on a hot plate. Fume 1 to 2 min. over an open flame and then 10 min. more on a hot plate. Cool somewhat, add 50 ml. of water, and transfer to a 600-ml. beaker. Add 20 ml. of  $\text{H}_2\text{SO}_4$ , dilute to 300 ml., and complete the determination as described in Section 1.

### THE COLORIMETRIC METHOD

**Reagents.** (a) Sodium Hydroxide-Sodium Sulfate Wash Solution.—Dissolve 20 g. of NaOH and 10 g. of  $\text{Na}_2\text{SO}_4$  in 1 liter of water.

(b) Standard Potassium Dichromate Solution (1 ml. = 0.0001 g. Cr).

(c) Color Standards.—Prepare solutions containing approximately the same concentrations of chromium and alkali as the solution of the sample that is to be compared with them. Solutions containing from 2 to 10 g. of NaOH and 1 mg. of chromium per 100 ml. are suitable. The color standards should be freshly prepared before using.

**Procedure.** 1. *Carbon Steels and Other Steels Containing Under 0.15% Chromium.*—(a) Transfer 10 g. of the sample<sup>65</sup> to a 500-ml. Erlenmeyer flask and add 110 ml. of  $\text{H}_2\text{SO}_4$  (exactly 1:9). Heat to boiling, boil until reaction is complete, and then dilute with 100 ml. of boiling water. Add  $\text{NaHCO}_3$  (80 g. per liter) from a buret until a permanent precipitate appears (approximately 36 ml. with carbon steels) and then 4 ml. in excess. Boil for 1 min., let settle, filter on a rapid filter, quickly wash the flask, and precipitate 2 or 3 times with hot water. If the precipitation has been properly performed, there will be no more precipitate than can be conveniently handled on an 11-cm. paper. The filtrate will become cloudy in the funnel stem and in the receiving vessel on account of oxidation and hydrolysis.

(b) Ignite the residue in a nickel or iron crucible (low in chromium) and fuse with 10 or 12 times its volume of  $\text{Na}_2\text{O}_2$  (low in chromium). Dissolve the cooled melt by immersing it in 100 ml. of cold water. Remove the crucible, add 1 g. of  $\text{Na}_2\text{O}_2$ , and boil for 5 to 10 min., or allow to stand on a steam bath for 30 min. Filter through an asbestos pad,<sup>66</sup> preferably on a small Büchner funnel, and wash with cold NaOH- $\text{Na}_2\text{SO}_4$  wash solution.

(c) Dilute to a measured volume and compare the color with color standards containing approximately the same concentration of chromium and alkali.

<sup>65</sup> Larger or smaller samples may be taken, but the volume of acid shall be varied accordingly. A good rule to follow is to use the equivalent of 1 ml. of  $\text{H}_2\text{SO}_4$  for each 1 g. of steel and then add 1 ml. in excess.

<sup>66</sup> Asbestos is more satisfactory than filter paper. If paper is used, it shall first be washed thoroughly with a solution of NaOH (50 g. per liter) in order to remove soluble organic matter.

(d) If the color of the unknown solution is too deep for convenient colorimetric comparison, the solution may be boiled thoroughly to decompose all the peroxide, acidified, and titrated as described in Paragraph (c) of the Persulfate Procedure.

**2. Cast Iron Containing Under 0.15% Chromium, Open-Hearth Iron, Wrought Iron, and High-Silicon Steels.**—Determine chromium in accordance with the procedure described in Section 1.

## VANADIUM

### THE ELECTROLYTIC SEPARATION METHOD

**Apparatus.**—The mercury cathode separation serves as a means of quantitatively removing iron, chromium, zinc, nickel, cobalt, tin, molybdenum, copper, bismuth, silver, and other ions from solution.<sup>67</sup> Only partial separations of manganese, antimony, arsenic, and ruthenium are obtained.<sup>68</sup> The separation is accomplished by reducing the ions electrolytically and causing them to amalgamate with the mercury pool that serves as cathode. Electrolysis is generally carried out in a sulfuric acid or perchloric acid solution that is free of chlorides and nitrates. The presence of large quantities of salt is undesirable because it slows down the reduction process. The most rapid electrolysis is obtained if the solution pH is about 1.5 and if solution and mercury are stirred during the process. The d.c. current should be 3 to 5 amp. with a voltage of 6 to 15 across each cell.

A simplified form of mercury cathode cell consists of a 400-ml. beaker containing 30 to 50 ml. of mercury to act as the cathode, and a platinum wire ring to act as the anode. The mercury is connected to the negative terminal by means of a mercury-filled, platinum-tipped glass-tubing electrode. The anode is placed as close to the surface of the solution as possible. A suitable source of direct current is required.

A more convenient form of the apparatus is that recommended by Melaven,<sup>69</sup> and is shown in Fig. 24-9. With this apparatus, the electrolyte is removed from the cell through the stopcock, which eliminates the necessity of siphoning off the solution, as is required with the simplified cell.

**Reagents.** (a) **Potassium Ferricyanide Solution.**—Prepare a very dilute solution as needed by dissolving a crystal the size of the head of a pin in 25 ml. of water.

(b) **Potassium Permanganate Solution (25 g. per liter).**

(c) **Standard Potassium Permanganate Solution (0.03 N).**

**Procedure. 1. Vanadium Steels.**—(a) Transfer 2 g. of the sample to a 300-ml. Erlenmeyer flask, and add 30 ml. of  $\text{H}_2\text{SO}_4$  (exactly 1:9). When action is complete, dilute to 100 ml. with boiling water and heat to boiling. Agitate gently while adding  $\text{NaHCO}_3$  (80 g. per liter) from a buret until a permanent precipitate is formed, and then add 4 ml. more. Cover the flask, boil for 1 min., and let the precipitate settle. Filter rapidly, conveniently by moderate suction through a cone and paper containing some paper pulp, and wash the flask and precipitate 4 or 5 times with hot water. The filtrate will become cloudy in the funnel stem

<sup>67</sup> Lundell, G. E. F., and Hoffman, J. I., *Outlines of Methods of Chemical Analysis*, John Wiley and Sons, Inc., New York, 94, 1938.

<sup>68</sup> Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd Ed., John Wiley and Sons, Inc., New York, 138-41, 1953.

<sup>69</sup> Melaven, A. D., *Electrolytic Cell for Use with the Mercury Cathode*, *Ind. Eng. Chem., Anal. Ed.*, 2, 180, 1930.



and receiving vessel because of oxidation and hydrolysis of the iron, but this is of no consequence.

(b) Place the paper and precipitate in the original flask, add 5 ml. of  $\text{H}_2\text{SO}_4$ , warm, and shake until the paper has broken up. Add 20 ml. of  $\text{HNO}_3$  and heat over a free flame to dense white fumes. Cool and, if organic matter is still present,

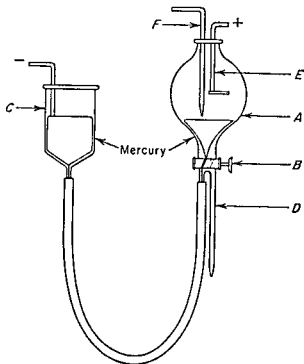


FIG. 24-9 Melaven Type Mercury Cathode Cell. *A*, glass vessel; *B*, two-way stopcock, wide-bore; *C*, leveling bulb; *D*, glass tubing constricted in same manner as a buret tip; *E*, platinum gauze or coiled platinum wire; *F*, narrow glass tube for introduction of air to stir the electrolyte and mercury (a motor-driven stirrer can be used instead)

add more  $\text{HNO}_3$  and repeat the treatment. Finally cool, wash down the flask, and repeat the evaporation to dense white fumes to ensure the complete elimination of  $\text{HNO}_3$ . Cool, dilute to 40 ml.,<sup>70</sup> neutralize the solution with  $\text{NH}_4\text{OH}$ ,

<sup>70</sup> If tungsten is present, the solution must be filtered, the tungstic acid washed with  $\text{H}_2\text{SO}_4$  (1:99), and its vanadium content determined colorimetrically and added to that found by titration. The colorimetric test shall be made as follows: dissolve the tungstic acid in a solution of  $\text{NaOH}$ , or fuse the ignited impure oxide with  $\text{Na}_2\text{CO}_3$  and extract the melt with water; filter if not clear, and dilute to 75 to 100 ml.; add  $\text{H}_3\text{PO}_4$  (1:1) until acid, then a 5-ml. excess, and let stand for 1 to 2 hr.; compare the yellow solution of vanadotungstic acid with a standard prepared by adding from a buret a standard solution of vanadotungstic acid to water until the intensity of color in the solution is the same when the solutions are of equal volume. The standard solution of vanadotungstic acid shall be prepared as follows: dissolve 2.5 g. of sodium tungstate and enough sodium vanadate to give exactly 0.05 g. of vanadium in 100 ml. of water; dilute to 200 ml.; add 25 ml. of  $\text{H}_3\text{PO}_4$  (1:1); and dilute to exactly 500 ml. Ammonium salts cannot be used as they give rise to turbid solutions. If only ammonium vanadate is available, dissolve it in water, expel all ammonia by boiling with a slight excess of  $\text{NaOH}$ , and acidify with  $\text{H}_3\text{PO}_4$ . The vanadium held by the tungsten approximates 0.01 mg. of vanadium per 0.01 g. of tungsten, and in routine analyses the correction is made by calculation, that is, 0.018% vanadium is added for an 18% tungsten steel.

add  $\text{H}_2\text{SO}_4$  until acid, and then add an excess of 0.5 ml. of  $\text{H}_2\text{SO}_4$  per 100 ml. of solution.

(c) Transfer the solution to a mercury cathode cell, rinsing the flask with small portions of water. The cathode wire shall be embedded in about 200 g. of mercury, and the solution electrolyzed at a current density of approximately 0.16 amp. per sq. cm. while stirring or agitating the solution. Continue the electrolysis until iron is absent, as indicated by a ferricyanide test on a small drop of the electrolyte. This should not require more than 45 min. When *all* the iron has been removed, draw off the electrolyte, and wash the mercury two or three times with water while continuing the current.<sup>71</sup> In these operations care shall be taken to prevent any amalgam from passing into the electrolyte.<sup>72</sup>

(d) Add 2 to 3 ml. of  $\text{H}_2\text{SO}_4$  (1:1), heat to  $70^\circ$  to  $80^\circ\text{C}$ ., and add  $\text{KMnO}_4$  (25 g. per liter) until a deep pink color appears. Heat to boiling, and pass a current of  $\text{SO}_2$  into the solution until the vanadium is reduced (2 to 5 min.).<sup>73</sup> Continue the boiling, and pass a rapid stream of  $\text{CO}_2$  (free of  $\text{O}_2$ ) through the solution until it is free of  $\text{SO}_2$ . This may be ascertained by passing the gas issuing from the flask into 5 ml. of water containing a drop of  $\text{H}_2\text{SO}_4$  (1:1) and enough  $\text{KMnO}_4$  to give a faint pink tint.

(e) Cool the solution to  $60^\circ$  to  $80^\circ\text{C}$ ., and titrate with 0.03 N  $\text{KMnO}_4$ . Repeat the reduction and titration until concordant results are obtained.

(f) **Blank.**—Correct the titration by a blank determination (usually amounting to about 0.1 ml. of 0.03 N  $\text{KMnO}_4$ ) on a solution of like volume and acidity.

(g) **Calculation.**—Calculate the percentage of vanadium as follows:

$$\text{Vanadium, per cent} = \frac{(A - B)C \times 0.051}{D} \times 100$$

where  $A$  = milliliters of  $\text{KMnO}_4$  solution required to titrate the sample,

$B$  = milliliters of  $\text{KMnO}_4$  solution required to titrate the blank,

$C$  = normality of the  $\text{KMnO}_4$  solution, and

$D$  = grams of sample used.

**2. Carbon Steels, Cast Iron, Open-Hearth Iron, and Wrought Iron.**—Determine vanadium in accordance with the procedure described in Section 1, except that 5 g. of the sample shall be dissolved in 60 ml. of  $\text{H}_2\text{SO}_4$  (exactly 1:9).

<sup>71</sup> To clean the mercury, transfer it to a large flask, add diluted  $\text{HNO}_3$  (1:9) containing a little  $\text{NaNO}_2$ , and agitate the mercury by drawing air through it for several hours. Remove the acid, add a fresh portion of acid, and agitate again. Draw off the second portion of acid, add water, and repeat the agitation. Repeat the treatment with water to remove all acid.

<sup>72</sup> With chromium steels it is usually necessary, because of the brittle chromium amalgam, to filter the electrolyte through a rapid filter and wash with water.

<sup>73</sup> The direct use of a solution of  $\text{H}_2\text{SO}_3$  or an alkali sulfite is unwise unless it has been freshly prepared, for after a lapse of time they contain oxidizable matter other than  $\text{H}_2\text{SO}_3$  or a sulfite. Sulfur dioxide is most conveniently used from a cylinder of the liquefied gas, or it may be obtained as wanted by heating a flask containing a solution of  $\text{H}_2\text{SO}_3$  or a sulfite to which  $\text{H}_2\text{SO}_4$  (1:1) is added.

# REDUCTION WITH FERROUS SULFATE AND TITRATION WITH PERMANGANATE <sup>74</sup>

**Reagents.** (a) Standard Ferrous Ammonium Sulfate Solution (0.03 N).

(b) Potassium Ferricyanide Solution.

(c) Ammonium Persulfate Solution (150 g. per liter).

(d) Standard Potassium Permanganate Solution (0.03 N).

(e) Cupferron Solution (60 g. per liter).—Dissolve 6 g. of cupferron in 80 ml. of cold water, dilute to 100 ml., and filter. This reagent shall be freshly prepared as needed.

**3. Chromium-Vanadium Steels.**—(a) To the solution reserved from the determination of chromium, add 5 ml. of  $\text{H}_3\text{PO}_4$ , unless the solution already contains it, and then add 15 ml. of 0.03 N ferrous ammonium sulfate (1 ml. will reduce 0.0015 g. of vanadium) if vanadium is under 0.8% and proportionately more if the percentage exceeds this amount. If enough has been added, a drop of the solution will give immediately a blue color with a drop of fresh  $\text{K}_3\text{Fe}(\text{CN})_6$  solution. Stir the solution thoroughly, add 8 ml. of freshly prepared  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (150 g. per liter), and stir for 1 min. Titrate with 0.03 N  $\text{KMnO}_4$  to a definite pink tint that does not fade upon continued stirring for 1 min.

(b) Blank.—Subtract the same blank as was obtained in the determination of chromium. If a correction for the end point has not been determined in a prior determination of chromium, the blank shall be obtained at this point as follows: boil the solution for 10 to 12 min. to destroy the slight excess of  $\text{KMnO}_4$ ; cool to room temperature; and titrate with 0.03 N  $\text{KMnO}_4$  to the same tint as was obtained before. The volume required represents the blank.<sup>75</sup> The vanadium may then again be reduced by an excess of ferrous ammonium sulfate and the solution treated with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , etc., as a check on the first titration.

(c) Calculation.—Calculate the percentage of vanadium as follows:

$$\text{Vanadium, per cent} = \frac{(A - B)C \times 0.051}{D} \times 100$$

where  $A$  = milliliters of  $\text{KMnO}_4$  solution required to titrate the sample,

$B$  = milliliters of  $\text{KMnO}_4$  solution required to titrate the blank,

$C$  = normality of the  $\text{KMnO}_4$  solution, and

$D$  = grams of sample used.

**4. Chromium-Tungsten-Vanadium Steels.**—(a) Transfer 2 g. of the sample to a 600-ml. beaker, and add 100 ml. of  $\text{H}_2\text{SO}_4$  (1:9). Heat until action ceases, add 10 ml. of  $\text{HNO}_3$  (1:1) and 4 ml. of  $\text{HCl}$  (1:1), and boil the solution gently for about 30 min. or until the tungsten has been oxidized to yellow tungstic acid. Stir frequently to break up the film adhering to the sides and bottom of the beaker.

<sup>74</sup> Where apparatus for potentiometric titration is available (Figs 24-5 and 24-6), oxidation with  $\text{HNO}_3$  is a very satisfactory method for the determination of vanadium, particularly for chromium-tungsten-vanadium steels. The sample is treated with 100 ml. of  $\text{H}_2\text{SO}_4$  (1:4) and then with  $\text{HNO}_3$  to oxidize iron (and tungsten). After dilution to 200 ml. and addition of 40 ml. of  $\text{HNO}_3$ , the solution is boiled for 1 hr. at such a rate that the volume will not drop below 100 ml., or preferably 115 ml., cooled to 8° to 10°C., diluted to 300 ml., and titrated potentiometrically with ferrous ammonium sulfate.

<sup>75</sup> The blank may also be obtained by means of a standard steel of known vanadium content and containing about the same amount of chromium as the test sample.

Dilute to 100 ml., filter through a close-texture paper, and wash with  $\text{H}_2\text{SO}_4$  (1:200).<sup>70</sup> Dilute the filtrate to 300 ml., add 5 ml. of  $\text{H}_3\text{PO}_4$ , and then add  $\text{KMnO}_4$  until the solution is pink.

(b) Add 15 ml. of 0.03 *N* ferrous ammonium sulfate and complete the determination as described in Section 3.

**5. Carbon Steels Containing Under 0.05% Vanadium.**—Transfer 10 g. of the sample to a 500-ml. Erlenmeyer flask, make a bicarbonate separation, fuse, and dissolve the melt as described in Section 1 (a) and (b) of the colorimetric method for chromium, p. 702. Acidify with  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  and complete the titration as described in Section 3.

**6. High-Chromium, High-Nickel Steels.**—(a) Transfer 10 g. of the sample (under 0.05% vanadium) to a 400-ml. beaker, add 250 ml. of  $\text{H}_2\text{SO}_4$  (1:9), and heat gently until action ceases. (For vanadium steels, use 2 g. of the sample and 150 ml. of  $\text{H}_2\text{SO}_4$  (5:95).) Cool the solution to 15°C., dilute to 500 ml. with water at the same temperature, and add two pieces of paper pulp  $\frac{1}{8}$  in. thick by 1 in. square, macerating the paper thoroughly. Then add drop by drop, while stirring constantly, cold cupferron (60 g. per liter) until the precipitate just assumes a reddish brown color. Filter through an 11-cm. paper containing some paper pulp, and wash 10 to 12 times with cold  $\text{H}_2\text{SO}_4$  (1:99).

(b) Transfer the paper and contents to the original beaker, and add 20 ml. of  $\text{HNO}_3$  and 10 ml. of  $\text{H}_2\text{SO}_4$ . Evaporate to dense white fumes. Cool, add 10 ml. of  $\text{HNO}_3$ , and again evaporate to dense white fumes. Cool, dilute to 300 ml., add 3 ml. of  $\text{H}_3\text{PO}_4$  (85%), and then add  $\text{KMnO}_4$  until the solution is pink.

(c) Add 15 ml. of 0.03 *N* ferrous ammonium sulfate and complete the determination as described in Section 3.

**7. Cast Iron Containing Under 0.05% Vanadium, Open-Hearth Iron, Wrought Iron, and High-Silicon Steels.**—Determine vanadium in accordance with the procedure described in Section 5.

## MOLYBDENUM

### THE ALPHA-BENZOINOXIME METHOD <sup>76</sup>

**Reagents.** (a) Boric Acid Solution (40 g. per liter).

(b) Alcohol Solution of alpha-Benzoinoxime (20 g. per liter).—Dissolve 10 g. of alpha-benzoinoxime in 500 ml. of ethanol or methanol. Filter if not clear.

(c) Alpha-Benzoinoxime Wash Solution.—Dilute 25 to 50 ml. of alpha-benzoinoxime (20 g. per liter) to 1 liter with cold  $\text{H}_2\text{SO}_4$  (1:99). This solution shall be freshly prepared before using.

(d) Cinchonine Solution.—Dissolve 125 g. of cinchonine in 1 liter of  $\text{HCl}$  (1:1).

(e) Cinchonine Wash Solution.—Dilute 30 ml. of cinchonine solution to 1 liter.

**Procedure. 1. Molybdenum Steels.**—(a) Transfer 1 to 3 g. of the sample to a 600-ml. beaker, add 50 ml. of  $\text{H}_2\text{SO}_4$  (1:6), and warm until action ceases. Carefully add just enough  $\text{HNO}_3$  to decompose carbides and to oxidize iron and molybdenum. Add 2 to 4 drops of  $\text{HF}$ , mix, and then add 10 ml. of boric acid (40 g. per

<sup>76</sup> Knowles, H. B., The Use of  $\alpha$ -Benzoinoxime in the Determination of Molybdenum, Nat. Bureau of Standards, Research Paper RP453, Journal of Research, 9, No. 1, 1, July, 1932.

liter).<sup>77</sup> Boil for a few minutes, and filter if the solution is not perfectly clear.<sup>78</sup>

(b) With some chromium steels, the acid-insoluble residue may contain small amounts of molybdenum. In this case, filter, ignite at as low a temperature as possible, and fuse slowly (below 500°C.) with  $K_2S_2O_7$ . Dissolve the melt in the main solution.

(c) Dilute to 100 ml. with water, cool to 25°C., and add sufficient  $FeSO_4$  (0.5 g is usually sufficient) to reduce vanadic and chromic acids. Cool to 5°C., stir, and slowly add 10 ml. of the ethanol solution of alpha-benzoinoxime (20 g. per liter) and then 5 ml. more for each 0.01 g. of molybdenum present. Continue to stir the solution, add 5 to 10 ml. of bromine water, and then add a few more milliliters of the alpha-benzoinoxime solution. Allow the beaker and contents to remain in the cooling mixture 10 min., while stirring occasionally. Stir in a little macerated filter pulp, and filter through a rapid paper. If the first 50 ml. or so are not entirely clear, filter this portion again. Wash the precipitate with 200 ml. of cold alpha-benzoinoxime wash solution. On standing, needlelike crystals will appear in the filtrate if sufficient reagent has been used.

(d) Transfer the precipitate and paper to a platinum crucible and dry cautiously. Char, without inflaming, and ignite at 500° to 525°C. Cool, weigh, and repeat the heating until the weight remains constant. Treat the ignited residue with 5 ml. of  $NH_4OH$ , digest, and filter through a small paper. Wash well with  $NH_4OH$  (1:99). Ignite the paper and contents in the original crucible, cool, and weigh. The difference in weights represents the  $MoO_3$  present.

(e) Tungsten is also precipitated. If present, the ammoniacal filtrate shall be treated as follows: Add 5 ml. of  $H_2SO_4$  (1:1) and evaporate to dense white fumes. Cool, dilute to 25 ml. with water, and add 1 to 2 ml. of cinchonine solution. Digest at 80° to 90°C., or preferably overnight at room temperature. Filter through a close-texture paper containing a little paper pulp and wash with cinchonine wash solution. Transfer the paper and contents to a platinum crucible, char the paper, and ignite at 750° to 850°C. to constant weight. Cool and weigh. In very accurate work, dissolve any residue obtained here and test for molybdenum by the colorimetric method.

(f) *Calculation.*—Calculate the percentage of molybdenum as follows:

$$\text{Molybdenum, per cent} = \frac{(A - B) \times 0.667}{C} \times 100$$

where  $A$  = grams of  $MoO_3$  (Paragraph (d)),

$B$  = correction for impurities (Paragraph (e)), in grams, and

$C$  = grams of sample used.

(g) With high-molybdenum, medium-tungsten steel (8% molybdenum, 2% tungsten) the ignited oxides may be weighed, dissolved, and molybdenum determined by the  $MoS_3$ - $MoO_3$  method (after reprecipitation of the sulfide). Tungsten is then obtained by difference.

<sup>77</sup> With larger samples (5 to 6 g) of silicon steel, it is best to evaporate the solution, dehydrate, and remove  $SiO_2$  before treatment with the alpha-benzoinoxime.

<sup>78</sup> If the sample is insoluble in this treatment, it may be dissolved in a mixture of  $HCl$  and  $HNO_3$ ,  $HClO_4$  added, and the solution evaporated to white fumes. The solution is then diluted and sufficient  $H_2SO_4$  added to reduce the chromium. After boiling out the excess  $SO_2$  and filtering off any silica, the solution is cooled and molybdenum then precipitated.

(h) If molybdenum is present in very small amounts (carbon steels), the ignited alpha-benzoinoxime precipitate shall be dissolved in  $\text{NH}_4\text{OH}$  and the molybdenum determined by the Photometric Method.

2. *Cast Iron*.—(a) Transfer 1 to 5 g. of the sample to a 600-ml. beaker, add 100 ml. of  $\text{H}_2\text{SO}_4$  (1:4), and warm. When action ceases, add  $\text{HNO}_3$  drop by drop until rapid effervescence ceases (usually 2 to 5 ml.), and then add 2 to 3 drops in excess. Evaporate the solution to dense white fumes, cool somewhat, and add 100 ml. of water. Warm until salts are dissolved and filter through a rapid paper. Wash the paper with warm water.

(b) Dilute the filtrate to 150 ml. and cool to  $25^\circ\text{C}$ . Add sufficient  $\text{FeSO}_4$  to reduce any chromium or vanadium that may have been oxidized by the above treatment, cool to  $5^\circ\text{C}$ ., and complete the determination as described in Section 1.

3. *Open-Hearth Iron and Wrought Iron*.<sup>79</sup>—Determine molybdenum in accordance with the procedure described in Section 1.

## PRECIPITATION AS SULFIDE AND WEIGHING AS OXIDE

*Reagents*. (a) Ammonium Persulfate Solution (250 g. per liter).

(b) Hydrogen Sulfide Wash Solution.—Saturate  $\text{H}_2\text{SO}_4$  (1:99) with  $\text{H}_2\text{S}$ .

*Procedure*. 1. *Molybdenum Steels Containing No Tungsten*.—(a) Transfer 2 to 10 g. of the sample (approximately 0.03 g. of molybdenum) to a 600-ml. beaker, add 100 ml. of  $\text{H}_2\text{SO}_4$  (1:5), and warm. When action ceases, add 20 ml. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (250 g. per liter) and boil the solution for 8 to 10 min. to oxidize the molybdenum and part of the iron. Cool somewhat, add 5 g. of tartaric acid, neutralize with  $\text{NH}_4\text{OH}$ , and add  $\text{H}_2\text{SO}_4$  (1:1) until acidified and then 10 ml. in excess for each 100 ml. of solution.

(b) Heat to boiling and pass in a rapid stream of  $\text{H}_2\text{S}$  for 10 min. Dilute with an equal volume of hot water, and pass in  $\text{H}_2\text{S}$  for 5 min. Digest at  $50^\circ$  to  $60^\circ\text{C}$ . for 1 hr. Filter, and wash the sulfur and sulfides with  $\text{H}_2\text{S}$  wash solution.<sup>80</sup>

(c) Place the paper and precipitate in the original beaker, add 5 ml. of  $\text{H}_2\text{SO}_4$  and 20 ml. of  $\text{HNO}_3$ , cover, and heat to dense white fumes. Cool somewhat, add 10 ml. of  $\text{HNO}_3$ , and again evaporate to dense white fumes. If the solution is not clear and of a light color, repeat the treatment with  $\text{HNO}_3$ . Cool, dilute to 100 ml., and add a slight excess (10 to 12 drops) of  $\text{NaOH}$  (200 g. per liter). Heat to boiling and set aside for 5 min. Filter, and wash the paper and residue with hot water.

(d) Heat the filtrate to boiling and pass in  $\text{H}_2\text{S}$  for 10 min. Add  $\text{H}_2\text{SO}_4$  (1:1) until acidified and then a 4-ml. excess per 100 ml. of solution. Pass  $\text{H}_2\text{S}$  into the solution for 5 min. and digest at  $50^\circ$  to  $60^\circ\text{C}$ . for 1 hr. Filter through a 9-cm. close-texture paper, and wash thoroughly with  $\text{H}_2\text{S}$  wash solution.<sup>81</sup>

<sup>79</sup> The small amounts of molybdenum normally encountered in these materials are preferably determined by the photometric method described below.

<sup>80</sup> In umpire analyses the filtrate shall be boiled to expel  $\text{H}_2\text{S}$  and its molybdenum content determined colorimetrically, or the unprecipitated molybdenum (usually not in excess of 0.5 mg.) shall be recovered as follows: boil the filtrate to expel  $\text{H}_2\text{S}$  and to reduce the volume to about 450 ml.; add 20 ml. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (250 g. per liter); boil for 8 to 10 min., and then pass in a rapid stream of  $\text{H}_2\text{S}$  for 10 to 15 min.; digest for 1 hr., filter, wash, and combine with the main precipitate.

<sup>81</sup> Precipitation of molybdenum is usually complete, but it is well to test the filtrate by boiling to expel  $\text{H}_2\text{S}$ , oxidizing with bromine water, boiling to expel bromine, and again passing  $\text{H}_2\text{S}$  into the solution.

liter).<sup>77</sup> Boil for a few minutes, and filter if the solution is not perfectly clear.<sup>78</sup>

(b) With some chromium steels, the acid-insoluble residue may contain small amounts of molybdenum. In this case, filter, ignite at as low a temperature as possible, and fuse slowly (below 500°C.) with  $K_2S_2O_7$ . Dissolve the melt in the main solution.

(c) Dilute to 100 ml. with water, cool to 25°C., and add sufficient  $FeSO_4$  (0.5 g. is usually sufficient) to reduce vanadic and chromic acids. Cool to 5°C., stir, and slowly add 10 ml. of the ethanol solution of alpha-benzoinoxime (20 g. per liter) and then 5 ml. more for each 0.01 g. of molybdenum present. Continue to stir the solution, add 5 to 10 ml. of bromine water, and then add a few more milliliters of the alpha-benzoinoxime solution. Allow the beaker and contents to remain in the cooling mixture 10 min., while stirring occasionally. Stir in a little macerated filter pulp, and filter through a rapid paper. If the first 50 ml. or so are not entirely clear, filter this portion again. Wash the precipitate with 200 ml. of cold alpha-benzoinoxime wash solution. On standing, needlelike crystals will appear in the filtrate if sufficient reagent has been used.

(d) Transfer the precipitate and paper to a platinum crucible and dry cautiously. Char, without inflaming, and ignite at 500° to 525°C. Cool, weigh, and repeat the heating until the weight remains constant. Treat the ignited residue with 5 ml. of  $NH_4OH$ , digest, and filter through a small paper. Wash well with  $NH_4OH$  (1:99). Ignite the paper and contents in the original crucible, cool, and weigh. The difference in weights represents the  $MoO_3$  present.

(e) Tungsten is also precipitated. If present, the ammoniacal filtrate shall be treated as follows: Add 5 ml. of  $H_2SO_4$  (1:1) and evaporate to dense white fumes. Cool, dilute to 25 ml. with water, and add 1 to 2 ml. of cinchonine solution. Digest at 80° to 90°C., or preferably overnight at room temperature. Filter through a close-texture paper containing a little paper pulp and wash with cinchonine wash solution. Transfer the paper and contents to a platinum crucible, char the paper, and ignite at 750° to 850°C. to constant weight. Cool and weigh. In very accurate work, dissolve any residue obtained here and test for molybdenum by the colorimetric method.

(f) Calculation.—Calculate the percentage of molybdenum as follows:

$$\text{Molybdenum, per cent} = \frac{(A - B) \times 0.667}{C} \times 100$$

where  $A$  = grams of  $MoO_3$  (Paragraph (d)),

$B$  = correction for impurities (Paragraph (e)), in grams, and

$C$  = grams of sample used.

(g) With high-molybdenum, medium-tungsten steel (8% molybdenum, 2% tungsten) the ignited oxides may be weighed, dissolved, and molybdenum determined by the  $MoS_3$ - $MoO_3$  method (after reprecipitation of the sulfide). Tungsten is then obtained by difference.

<sup>77</sup> With larger samples (5 to 6 g.) of silicon steel, it is best to evaporate the solution, dehydrate, and remove  $SiO_2$  before treatment with the alpha-benzoinoxime.

<sup>78</sup> If the sample is insoluble in this treatment, it may be dissolved in a mixture of  $HCl$  and  $HNO_3$ ,  $HClO_4$  added, and the solution evaporated to white fumes. The solution is then diluted and sufficient  $H_2SO_4$  added to reduce the chromium. After boiling out the excess  $SO_2$  and filtering off any silica, the solution is cooled and molybdenum then precipitated.

(b) Add 5 g. of tartaric acid to the filtrate and neutralize the solution with  $\text{NH}_4\text{OH}$ . Add 10 ml. of  $\text{H}_2\text{SO}_4$  (1:1) for each 100 ml. of solution, heat to boiling, and pass in a rapid stream of  $\text{H}_2\text{S}$  for 10 min. Dilute with an equal volume of hot water, and pass in  $\text{H}_2\text{S}$  for 5 min. Digest at  $50^\circ$  to  $60^\circ\text{C}$ . for 1 hr. Filter, and wash the sulfur and sulfides with  $\text{H}_2\text{S}$  wash solution.

(c) Complete the determination as described in Section 1 (c) to (g).

4. *Carbon Steels, Open-Hearth Iron, and Wrought Iron*.—Determine molybdenum in accordance with the procedure described in Section 1.

## THE PHOTOMETRIC METHOD

**Reagents.** (a) Sodium Thiocyanate Solution (50 g. per liter).

(b) Stannous Chloride Solution (350 g. per liter).—Transfer 350 g. of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  to a 500-ml. Erlenmeyer flask, add 200 ml. of  $\text{HCl}$  (1:1), and warm ( $60^\circ$  to  $70^\circ\text{C}$ .) until solution is practically complete. Cool and dilute to 1 liter in a volumetric flask with freshly boiled and cooled water. Add a few pieces of metallic tin, and stopper.

(c) Butyl Acetate or Isopropyl Ether:

(1) Saturate technical butyl acetate with  $\text{NaCNS}$  and  $\text{SnCl}_2$  by shaking; keep in a dark bottle.

(2) Shake 50 ml. of butyl acetate or isopropyl ether with 25 ml. of  $\text{Fe}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  (80 g. per liter), 10 ml. of  $\text{NaCNS}$  (50 g. per liter), and 10 ml. of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (350 g. per liter). Draw off and discard the lower or acid layer. Prepare the butyl acetate or isopropyl ether by this method immediately prior to use.

(d) Ferric Sulfate Solution (80 g. per liter).—Dissolve 80 g. of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  in water and dilute to 1 liter.

(e) Standard Molybdenum Solution (1 ml. = 0.0002 g. Mo).—Dissolve 0.5 g. of pure  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  in 1 liter of water containing 5 ml. of  $\text{H}_2\text{SO}_4$ . Aliquots of this solution may be diluted to suitable strength for use.

**Standardization.**—Standardize in accordance with either method A or B.

**Method A (Volumetric).**—Pipet 100 ml. of the molybdenum solution into a 250-ml. beaker, add 10 ml. of  $\text{H}_2\text{SO}_4$  (1:1), and reduce in the Jones reductor as described below. If the Jones reductor has been standing idle, pass 100 ml. of  $\text{H}_2\text{SO}_4$  (5:95) through it, then some water, and discard the wash solution. Add 30 ml. of ferric phosphate solution to the receiver, and then enough water so that the tip of the reductor dips beneath the surface of the solution. (To prepare the ferric phosphate solution, dissolve 100 g. of  $\text{Fe}_2(\text{SO}_4)_3$  in 1 liter of water to which 150 ml. of  $\text{H}_3\text{PO}_4$  and 20 ml. of  $\text{H}_2\text{SO}_4$  (1:1) have been added. Add  $\text{KMnO}_4$  (25 g. per liter) until the solution is just tinted pink.) Draw the molybdenum solution, by gentle suction, through the reductor. Just before the surface of the liquid reaches the zinc, add a 50-ml. portion of water, and finally rinse by adding two more 50-ml. portions each time just before the surface of the solution reaches the zinc. Close the stopcock, disconnect, and raise the reductor as a little water is allowed to run through the stem. Rinse the stem and titrate the solution with 0.1 N  $\text{KMnO}_4$ . Make a blank determination, following the same procedure and using the same amounts of all reagents.

**Method B (Gravimetric).**<sup>83a, 83b</sup>—Pipet 25 ml. of the molybdenum solution into a 250-ml. beaker and dilute to 150 ml. Add 1 drop of methyl orange indicator (1 g.

<sup>83a</sup> This procedure is based on the work of McCay, L. W., The Weighing of Molybdenum as Silver Molybdate, J., Am. Chem. Soc., 56, 2548, 1934.

<sup>83b</sup> The following method is recommended as an alternative gravimetric procedure for standardizing molybdenum solutions: Pipet 50 ml. of the molybdenum solution into a



(e) Transfer the precipitate to a small porcelain crucible, and heat carefully until carbon is destroyed and then at 500° to 525°C. to constant weight.<sup>82</sup> Weigh as  $\text{MoO}_3$ .

(f) Test the ignited oxide for impurities by treating with  $\text{NH}_4\text{OH}$ . If copper is indicated, determine its amount colorimetrically and calculate to  $\text{CuO}$ . If a residue remains, filter, wash with water, ignite, and weigh.<sup>83</sup>

(g) Calculation.—Calculate the percentage of molybdenum as follows:

$$\text{Molybdenum, per cent} = \frac{(A - B) \times 0.667}{C} \times 100$$

where  $A$  = grams of  $\text{MoO}_3$  (Paragraph (e)),

$B$  = correction for impurities (Paragraph (f)), in grams, and

$C$  = grams of sample used.

**2. Tungsten Steels.**—(a) Dissolve 2 to 10 g. of the sample (approximately 0.03 g of molybdenum) in 100 ml. of  $\text{HCl}$  (1:1), cautiously add 20 ml. of  $\text{HNO}_3$  (1:1), and then boil gently until the tungstic acid becomes bright yellow. Dilute to 150 ml. and heat to boiling. Filter, and wash the residue with  $\text{HCl}$  (1:9). Reserve the precipitate.

(b) Add 15 ml. of  $\text{H}_2\text{SO}_4$  to the filtrate, evaporate to fumes of  $\text{H}_2\text{SO}_4$ , cool, and add 100 ml. of water. Digest until soluble salts are in solution. If any tungstic acid separates, filter through a small filter, wash with a little  $\text{H}_2\text{SO}_4$  (1:99), and combine with the reserved tungstic acid precipitate (Paragraph (a)). Small amounts of tungsten will not precipitate, but will form a complex with the molybdenum and be held in solution.

(c) Add 5 g. of tartaric acid to the clear filtrate and neutralize with  $\text{NH}_4\text{OH}$ . Add  $\text{H}_2\text{SO}_4$  (1:1) until acidified, then 10 ml. in excess per 100 ml. of solution, and pass in  $\text{H}_2\text{S}$  as described in Section 1 (b).

(d) Some molybdenum is always carried down by the tungstic acid and shall be recovered as follows: dissolve the combined tungstic acid residues in a hot solution of  $\text{NaOH}$  (50 g. per liter), and wash the papers with a little water and then with a little hot  $\text{H}_2\text{SO}_4$  (1:99); add 5 g. of tartaric acid, then  $\text{H}_2\text{SO}_4$  until the solution contains 5 ml. per 100 ml., and precipitate with  $\text{H}_2\text{S}$  as described in Section 1 (b). Filter, wash, combine with the main sulfide precipitate, and complete the determination as described in Section 1 (c) to (g).

**3. Cast Iron.**—(a) Transfer 2 to 5 g. of the sample to a 600-ml. beaker, add 100 ml. of  $\text{H}_2\text{SO}_4$  (1:4), and warm. When action ceases, add  $\text{HNO}_3$  (1:1) drop by drop until rapid effervescence ceases (usually 5 to 10 ml.), and then add three to five drops in excess. Evaporate the solution to dense white fumes. Cool somewhat, add 100 ml. of warm water, stir, and heat until salts are dissolved. Filter through a rapid paper, catching the filtrate in a 600-ml. beaker. Wash the paper well with hot water.

<sup>82</sup> Molybdenum oxide volatilizes at temperatures above 500°C. but the rate is very slow at temperatures below 600°C. The heating may be done in a muffle, using a pyrometer for temperature control, or in a "radiator" consisting of a 50-ml. porcelain crucible containing a disc of asbestos board, 4 mm. thick on the bottom and fitted with a Nichrome triangle which is bent to fit the inside of the crucible and supported by bending the end wires over the rim. The crucible shall be placed so that the bottom is 8 cm. above the top of a Tirrill burner and heated by a flame 12.5 cm. high.

<sup>83</sup> If residual amounts of molybdenum are being determined, the determination shall be checked by testing the solution of the oxide as described in Paragraphs (c) to (e) of the Photometric Method procedure below.

(b) Add 5 g. of tartaric acid to the filtrate and neutralize the solution with  $\text{NH}_4\text{OH}$ . Add 10 ml. of  $\text{H}_2\text{SO}_4$  (1:1) for each 100 ml. of solution, heat to boiling, and pass in a rapid stream of  $\text{H}_2\text{S}$  for 10 min. Dilute with an equal volume of hot water, and pass in  $\text{H}_2\text{S}$  for 5 min. Digest at  $50^\circ$  to  $60^\circ\text{C}$ . for 1 hr. Filter, and wash the sulfur and sulfides with  $\text{H}_2\text{S}$  wash solution.

(c) Complete the determination as described in Section 1 (c) to (g).

4. *Carbon Steels, Open-Hearth Iron, and Wrought Iron*.—Determine molybdenum in accordance with the procedure described in Section 1.

## THE PHOTOMETRIC METHOD

**Reagents.** (a) Sodium Thiocyanate Solution (50 g. per liter).

(b) Stannous Chloride Solution (350 g. per liter).—Transfer 350 g. of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  to a 500-ml. Erlenmeyer flask, add 200 ml. of  $\text{HCl}$  (1:1), and warm ( $60^\circ$  to  $70^\circ\text{C}$ .) until solution is practically complete. Cool and dilute to 1 liter in a volumetric flask with freshly boiled and cooled water. Add a few pieces of metallic tin, and stopper.

(c) Butyl Acetate or Isopropyl Ether:

(1) Saturate technical butyl acetate with  $\text{NaCNS}$  and  $\text{SnCl}_2$  by shaking; keep in a dark bottle.

(2) Shake 50 ml. of butyl acetate or isopropyl ether with 25 ml. of  $\text{Fe}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  (80 g. per liter), 10 ml. of  $\text{NaCNS}$  (50 g. per liter), and 10 ml. of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (350 g. per liter). Draw off and discard the lower or acid layer. Prepare the butyl acetate or isopropyl ether by this method immediately prior to use.

(d) Ferric Sulfate Solution (80 g. per liter).—Dissolve 80 g. of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  in water and dilute to 1 liter.

(e) Standard Molybdenum Solution (1 ml. = 0.0002 g. Mo).—Dissolve 0.5 g. of pure  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  in 1 liter of water containing 5 ml. of  $\text{H}_2\text{SO}_4$ . Aliquots of this solution may be diluted to suitable strength for use.

**Standardization.**—Standardize in accordance with either method A or B.

**Method A (Volumetric).**—Pipet 100 ml. of the molybdenum solution into a 250-ml. beaker, add 10 ml. of  $\text{H}_2\text{SO}_4$  (1:1), and reduce in the Jones reductor as described below. If the Jones reductor has been standing idle, pass 100 ml. of  $\text{H}_2\text{SO}_4$  (5:95) through it, then some water, and discard the wash solution. Add 30 ml. of ferric phosphate solution to the receiver, and then enough water so that the tip of the reductor dips beneath the surface of the solution. (To prepare the ferric phosphate solution, dissolve 100 g. of  $\text{Fe}_2(\text{SO}_4)_3$  in 1 liter of water to which 150 ml. of  $\text{H}_3\text{PO}_4$  and 20 ml. of  $\text{H}_2\text{SO}_4$  (1:1) have been added. Add  $\text{KMnO}_4$  (25 g. per liter) until the solution is just tinted pink.) Draw the molybdenum solution, by gentle suction, through the reductor. Just before the surface of the liquid reaches the zinc, add a 50-ml. portion of water, and finally rinse by adding two more 50-ml. portions each time just before the surface of the solution reaches the zinc. Close the stopcock, disconnect, and raise the reductor as a little water is allowed to run through the stem. Rinse the stem and titrate the solution with 0.1 *N*  $\text{KMnO}_4$ . Make a blank determination, following the same procedure and using the same amounts of all reagents.

**Method B (Gravimetric).**<sup>83a, 83b</sup>—Pipet 25 ml. of the molybdenum solution into a 250-ml. beaker and dilute to 150 ml. Add 1 drop of methyl orange indicator (1 g.

<sup>83a</sup> This procedure is based on the work of McCay, L. W., The Weighing of Molybdenum as Silver Molybdate, J., Am. Chem. Soc., 56, 2548, 1934.

<sup>83b</sup> The following method is recommended as an alternative gravimetric procedure for standardizing molybdenum solutions: Pipet 50 ml. of the molybdenum solution into a

per liter) and then neutralize the solution with NaOH (200 g. per liter) until the indicator changes to a yellow tint. Add  $\text{H}_2\text{SO}_4$  (1:4) drop by drop until the pink color just returns. Dissolve 1 g. of sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ )<sup>83c</sup> in the solution (this should cause the indicator to change back to a yellow tint). Heat the solution just to the boiling point and precipitate by the addition of  $\text{AgNO}_3$  (20 g. per liter) drop by drop until an excess of several drops has been reached. Stir occasionally, while cooling to room temperature. A curdy precipitate that settles out completely, leaving a clear supernatant solution, should result. Filter on a weighed fritted-glass crucible with gentle suction and wash. All transferring and washing must be done with  $\text{AgNO}_3$  (5 g. per liter) because of the solubility of the precipitate in water. Finally wash 3 times with 5-ml. portions of ethanol (95%) in order to remove the last traces of  $\text{AgNO}_3$ . Dry at  $250^\circ\text{C}$ .<sup>83d</sup> and weigh as  $\text{Ag}_2\text{MoO}_4$ .

**Procedure.**—(a) Transfer 0.1 g. of the sample (for steels and irons containing from 0.02 to 0.4% molybdenum) to a 150-ml. Erlenmeyer flask. Add 10 ml. of  $\text{HClO}_4$  (1:1), warm until the sample has dissolved, and then add 1 ml. of  $\text{HNO}_3$ . Heat to boiling, cover, and fume until all carbonaceous matter has been destroyed. Cool somewhat, add 25 ml. of water, and boil for a few minutes to expel free chlorine. For steels and irons containing higher percentages of molybdenum, use proportionate amounts of sample and reagents.

(b) If the steel contains less than 0.02% of molybdenum, dissolve 0.5 to 1.0 g. of the sample in 20 ml. of  $\text{HNO}_3$  (1:3), add 8 ml. of  $\text{HClO}_4$ , and evaporate to fumes. In the case of high-silicon steel, add 0.5 ml. of HF before evaporating to white fumes. Cool, wash down the sides of the flask with water, and again evaporate to white fumes. Cool somewhat, add 25 ml. of water, and boil for a few minutes to expel free chlorine.

(c) To the cooled solution (Paragraph (a) or (b)), add 2 g. of tartaric acid and a slight excess of NaOH (200 g. per liter). About 30 ml. will be required. Heat to about  $80^\circ\text{C}$ . for a few minutes, remove from the source of heat, and cool somewhat. Neutralize to litmus with  $\text{H}_2\text{SO}_4$  (1:1), and then add an excess of 2 ml. for each 8 ml. of solution, which will give a solution containing 10% of  $\text{H}_2\text{SO}_4$  by volume. Cool the solution to  $25^\circ\text{C}$ . and transfer to a 250-ml. cylindrical-type separatory funnel, rinsing the flask twice with 5-ml. portions of cool  $\text{H}_2\text{SO}_4$  (1:9).

(d) Add 10 ml. of  $\text{NaCNS}$  (50 g. per liter) and shake 0.5 min. Add 10 ml. of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (350 g. per liter) (20 ml. for 1 g. of the sample), and shake vigorously

400-ml. beaker, dilute to 100 ml. with water, and add an excess of 2 ml. of HCl. Then add 50 ml. of ammonium acetate (500 g. per liter), heat to boiling, and while stirring constantly, slowly add 20 ml. of lead acetate (10 g. per liter) containing 10 ml. of acetic acid per liter. Boil for 5 min., allow the precipitate to settle, filter on a 9 cm. medium-texture paper containing a little ashless paper pulp, and wash 18 to 20 times with hot  $\text{NH}_4\text{NO}_3$  (25 g. per liter). Ignite in porcelain, first at a temperature of  $400^\circ$  to  $500^\circ\text{C}$ . to burn off the paper, and then for 10 to 15 min. (to constant weight) at approximately  $600^\circ\text{C}$ . Cool and weigh. Multiply the weight of  $\text{PbMoO}_4$  found by 0.2614 to obtain the weight of molybdenum in 50 ml. of solution.

The alpha-benzoinoxime method is also recommended as an alternative gravimetric method for standardizing molybdenum solutions; see the paper by Knowles, H. B., The Use of  $\alpha$ -Benzoinoxime in the Determination of Molybdenum, *Journal of Research, Nat. Bureau Standards*, Vol. 9, No. 1, July, 1932, p. 1. (Research Paper RP 453.)

<sup>83c</sup> Because of the limited solubility of silver acetate, this amount of 1 g. of sodium acetate should not be exceeded, although enough must be added to neutralize the solution (shown by the change in color of the indicator to yellow).

<sup>83d</sup> If the precipitate is dried at  $110^\circ\text{C}$ ., a few tenths of a milligram of water remains.

for 1 min. Add 50 ml. of butyl acetate<sup>84</sup> or preferably isopropyl ether (treated similarly) from a transfer pipet, stopper the funnel, and shake vigorously for several minutes. Allow the layers to separate; then draw off the lower acid layer. Next draw off the upper or ether layer into a 100-ml. volumetric flask. Return the acid layer to the separatory funnel, add 40 to 50 ml. of butyl acetate or isopropyl ether, stopper, and repeat the shaking. Draw off the lower layer and discard. Add the upper or ether layer to that in the 100-ml. volumetric flask and dilute to the mark with butyl acetate or isopropyl ether. Mix thoroughly and allow the solution in the flask to stand for 2 or 3 min.

(e) Transfer a portion of the clear extract<sup>85</sup> to an absorption cell and measure the absorbance or transmittance in a photoelectric photometer, using a green filter (540  $m\mu$ ) and a blank (on the reagents) to set the zero. Determine the percentage of molybdenum from a previously prepared calibration curve obtained by adding varying portions of standard molybdenum solution to molybdenum-free steels and proceeding as in the method.

## TUNGSTEN

### THE ACID DIGESTION-CINCHONINE METHOD

**Reagents.** (a) Cinchonine Solution (125 g. per liter).—Dissolve 125 g. of cinchonine in 1 liter of HCl (1:1) and filter.

(b) Cinchonine Wash Solution.—Dilute 30 ml. of cinchonine solution to 1 liter with water.

(c) Ammonium Chloride Wash Solution.—Dissolve 20 g. of  $\text{NH}_4\text{Cl}$  in 1 liter of water and add 1 or 2 drops of  $\text{NH}_4\text{OH}$ .

(d) Standard Molybdenum Solution (1 ml. = 0.0002 g. Mo).

**Procedure.** 1. *Tungsten Steels.*—(a) Transfer 2 g. (for steels containing less than 5% of tungsten use 5 g.) of the sample to a 400-ml. beaker,<sup>86</sup> cover, and add 50 ml. of HCl. Warm gently. When decomposition is complete, cease heating, and scrub with a policeman to detach carbides and tungsten. Gradually add 10 ml. of  $\text{HNO}_3$  (1:1). Digest at 100°C., with occasional stirring, until the tungstic acid is bright yellow and free of black particles. Dilute to 150 ml. and add 5 ml. of cinchonine solution and a small amount of paper pulp. Digest at 90° to 95°C. for 30 min. or longer, while stirring the solution occasionally.<sup>87</sup> With high-molybdenum steels, let stand for about 36 hr. in order to obtain complete precipitation of tungsten. Decant the clear solution through an ashless paper containing a little ashless paper pulp. Wash by decantation with two or three 30- to 40-ml. portions of hot cinchonine wash solution, transfer the residue to the paper,<sup>88</sup> and wash thoroughly with hot cinchonine wash solution.

(b) Transfer the paper and residue to a weighed platinum crucible, and ignite

<sup>84</sup> For satisfactory color comparisons the concentration of molybdenum should not exceed 0.03 mg. per milliliter of solvent. Extraction should be made immediately following addition of the  $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ .

<sup>85</sup> If the extract is turbid, allow to stand for about 10 min., or filter through a layer of glass wool.

<sup>86</sup> Smooth (unetched) beakers should be used, because tungstic acid has a tendency to stick rather tenaciously to the vessel.

<sup>87</sup> Small amounts of tungsten separate slowly in the presence of considerable iron. Consequently, with under 2% of tungsten, let the solution stand for 18 to 24 hr.

<sup>88</sup> Dissolve any  $\text{WO}_3$  that still adheres to the beaker by adding a few drops of  $\text{NH}_4\text{OH}$ . Evaporate just to dryness, and then add 2 to 3 ml. of HCl (1:9) and 0.5 ml. of cinchonine solution. Heat to boiling, digest a few minutes, and pour onto the filter.

at as low a temperature as possible until carbon is gone. Add 1 or 2 drops of  $\text{H}_2\text{SO}_4$  (1:1) and 1 to 3 ml. of HF. Evaporate to dryness, ignite at  $750^\circ$  to  $850^\circ\text{C}$ ., cool, and weigh as "impure  $\text{WO}_3$ ."

(c) Add 4 g. of  $\text{Na}_2\text{CO}_3$ , and heat gradually until fusion is complete. Cool, take up the melt in 100 ml. of water, and filter. Thoroughly wash the crucible and residue, and reserve the filtrate. Transfer the residue to the crucible, ignite, fuse with 1 g. of  $\text{Na}_2\text{CO}_3$ , cool, and take up in 25 ml. of water. Filter, and thoroughly wash the crucible, paper, and residue with hot water. Combine the filtrate with the reserved filtrate. Again transfer the residue to the crucible and ignite. Cool, weigh, correct for the residue obtained from 5 g. of  $\text{Na}_2\text{CO}_3$ ,<sup>89</sup> and subtract the corrected weight from the weight of "impure  $\text{WO}_3$ ."

(d) If the combined filtrates show a yellow color, evaporate to 100 ml. and determine chromium colorimetrically (as under the determination of chromium in carbon steels). Calculate to  $\text{Cr}_2\text{O}_3$ , and deduct from the weight of "impure  $\text{WO}_3$ ." Divide the solution into three equal parts. In one aliquot determine molybdenum oxide,  $\text{MoO}_3$ , by the colorimetric method. In the second aliquot determine vanadium pentoxide,  $\text{V}_2\text{O}_5$ , by the colorimetric method,<sup>90</sup> adding one third as much chromate to the comparison solution as was found in the colorimetric test. In the third aliquot separate tin, tantalum, niobium,<sup>91</sup> and the like by acidifying, adding  $\text{NH}_4\text{OH}$  in moderate excess, and boiling until the odor of ammonia is barely perceptible. Filter, wash thoroughly with hot  $\text{NH}_4\text{Cl}$  wash solution, ignite, and weigh. Add the weights of the oxides found in the three aliquots, multiply by 3, and subtract from the weight of the "impure  $\text{WO}_3$ ."

(e) Calculation.—Calculate the percentage of tungsten as follows:

$$\text{Tungsten, per cent} = \frac{A \times 0.793}{B} \times 100$$

where  $A$  = grams of  $\text{WO}_3$ , corrected as described in Paragraphs (c) and (d), and  $B$  = grams of sample used.

<sup>89</sup> The residue obtained from the c.p. grade of  $\text{Na}_2\text{CO}_3$  usually exceeds 1 mg. In analyses of 2-g. samples of a high-speed tool steel (18.23% tungsten, 3.51% chromium, and 0.97% vanadium), the correction for the impurities in the  $\text{Na}_2\text{CO}_3$  averaged 1 mg. and the impurities in the "impure  $\text{WO}_3$ " averaged 5.8 mg. (representing 0.23% of tungsten). The weights of  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{V}_2\text{O}_5$  that were obtained ranged from 1.4 to 4.4 mg., 0.4 to 0.5 mg., and 1.4 to 2.7 mg., respectively.

<sup>90</sup> If tungsten is present, the solution must be filtered, the tungstic acid washed with  $\text{H}_2\text{SO}_4$  (1:99), and its vanadium content determined colorimetrically and added to that found by titration. The colorimetric test shall be made as follows: dissolve the tungstic acid in a solution of  $\text{NaOH}$ , or fuse the ignited impure oxide with  $\text{Na}_2\text{CO}_3$  and extract the melt with water; filter if not clear, and dilute to 75 to 100 ml.; add  $\text{H}_3\text{PO}_4$  (1:1) until acid, then a 5-ml. excess, and let stand for 1 to 2 hr.; compare the yellow solution of vanadotungstic acid with a standard prepared by adding from a buret a standard solution of vanadotungstic acid to water until the intensity of color in the solution is the same when the solutions are of equal volume. The standard solution of vanadotungstic acid shall be prepared as follows: dissolve 2.5 g. of sodium tungstate and enough sodium vanadate to give exactly 0.05 g. of vanadium in 100 ml. of water; dilute to 200 ml.; add 25 ml. of  $\text{H}_3\text{PO}_4$  (1:1) and dilute to exactly 500 ml. Ammonium salts cannot be used as they give rise to turbid solutions. If only ammonium vanadate is available, dissolve it in water, expel all ammonia by boiling with a slight excess of  $\text{NaOH}$ , and acidify with  $\text{H}_3\text{PO}_4$ . The vanadium held by the tungsten approximates 0.01 mg. of vanadium per 0.01 g. of tungsten, and in routine analyses the correction is made by calculation, that is 0.018% vanadium is added for an 18% tungsten steel.

<sup>91</sup> If a search is to be made for tantalum and niobium, the residue insoluble in  $\text{Na}_2\text{CO}_3$  should also be examined, because part of these may be contained in it.

**2. Carbon Steels and Other Steels Containing Under 0.2% Tungsten.**—Transfer 5 g. of the sample to a 600-ml. beaker, add 75 ml. of  $\text{H}_2\text{SO}_4$  (1:6), and warm until action ceases. Carefully add just enough  $\text{HNO}_3$  (1:1) to decompose carbides and to oxidize the iron. Add about 5 mg. of molybdenum (conveniently, 25 ml. of molybdenum steels procedure). Determine tungsten subsequently in the mixed ox- and precipitate with alpha-benzoinoxime (see Paragraphs (c), (d), and (e) of the molybdenum steels procedure. Determine tungsten subsequently in the mixed oxides by precipitation with cinchonine as described in Section 1.

## COBALT

### THE ZINC OXIDE-ALPHA-NITROSO-BETA-NAPHTHOL METHOD

**Reagents.** (a) **Zinc Oxide Suspension.**—Add 50 g. of finely powdered ZnO to 300 ml. of water and shake thoroughly. Prepare fresh before using.

(b) **Alpha-Nitroso-beta-Naphthol Solution (70 g. per liter).**

**Procedure.** 1. **Cobalt Steels.**—(a) Transfer 1 g. of the sample to a 400-ml. beaker, add 25 ml. of  $\text{HCl}$  (1:1), heat, and when decomposition is complete, add 5 ml. of  $\text{HNO}_3$  (1:1) to oxidize the iron. If tungsten is present, the digestion with  $\text{HCl}$  and  $\text{HNO}_3$  shall be continued until all of the tungsten has been converted to yellow tungstic acid. Evaporate until salts begin to separate (about 5 ml.). Add 100 ml. of hot water, and digest on a steam bath for about 5 min. Dilute the solution to about 200 ml., and add ZnO suspension in portions of about 5 ml. until the iron is precipitated and a slight excess of ZnO is present. Shake thoroughly after each addition of the precipitant and avoid a large excess. When sufficient ZnO has been added, further addition of the reagent causes the brown precipitate to appear lighter in color upon thorough shaking. A sufficient excess is also indicated by a slightly white and milky supernatant liquid. Allow the precipitate to settle for a few minutes and filter the solution through a 12.5-cm. rapid paper.<sup>92</sup> Wash the beaker and the precipitate on the filter three times with cold water. Reserve the filtrate and washings.

(b) When the filter has drained, transfer the paper and precipitate to the beaker in which the precipitation was made, add 12 ml. of  $\text{HCl}$ , and stir the paper to a pulp. The iron should now be in solution; if it is not, add more  $\text{HCl}$ , avoiding a large excess. Dilute the solution to 200 ml., and repeat the precipitation with ZnO. Filter on a 15-cm. paper, and wash four or five times with cold water.

(c) To the combined filtrates and washings from the ZnO separation, add 10 ml. of  $\text{HCl}$ , and adjust the volume to about 400 ml. Heat the solution to boiling. Add 3 ml. of alpha-nitroso-beta-naphthol solution for each 0.01 g. of cobalt present and then 8 ml. more. Allow the solution to cool for 30 min. or more, and filter through a rapid paper. Transfer all of the precipitate to the paper, and wash with hot  $\text{HCl}$  (1:3) and then thoroughly with hot water.

(d) Transfer the wet paper and precipitate to a weighed porcelain crucible, heat gently at first, preferably in a muffle furnace, and finally ignite to constant weight at  $750^\circ$  to  $850^\circ\text{C}$ . Heating above  $900^\circ\text{C}$ . has a tendency to convert  $\text{Co}_3\text{O}_4$  to  $\text{CoO}$ . Cool, and weigh as  $\text{Co}_3\text{O}_4$ .<sup>93</sup> In very accurate work in which more than 0.01 g.

<sup>92</sup> A little finely divided ZnO may pass through the paper at first. This is unobjectionable, because zinc is not precipitated by alpha-nitroso-beta-naphthol.

<sup>93</sup> With high-molybdenum or copper steels (over 1%), the ignited  $\text{Co}_3\text{O}_4$ , or metallic cobalt, may contain small amounts (approximately 0.5 mg.) of these elements. Suitable cor-

of cobalt is involved, reduce the oxide in hydrogen, cool in an atmosphere of hydrogen, and weigh as metallic cobalt.

(e) Nickel accompanies cobalt almost completely in the zinc oxide separation. Hence, in very accurate work, when nickel predominates, or much of it is present, the ignited  $\text{Co}_3\text{O}_4$  should be dissolved in HCl and cobalt again precipitated with alpha-nitroso-beta-naphthol.<sup>94</sup>

(f) Blank.—Make a blank determination, following the same procedure and using the same amounts of all reagents. It is especially important that the same quantity of the alpha-nitroso-beta-naphthol be used in the blank determination as for the sample. A little macerated paper added to the blank after the alpha-nitroso-beta-naphthol reagent facilitates filtration and washing.

(g) Calculation.—Calculate the percentage of cobalt as follows:

$$\text{Cobalt, per cent} = \frac{(A - B) \times 0.734}{C} \times 100$$

where  $A$  = grams of  $\text{Co}_3\text{O}_4$ ,

$B$  = correction for blank, in grams, and

$C$  = grams of sample used.

**2. Carbon Steels and Other Steels Containing Under 0.10% Cobalt.**—Dissolve 10 g. of the sample in HCl and cautiously oxidize with just enough  $\text{HNO}_3$ . Extract the iron with ethyl ether and wash the ether extract once with HCl (1:1) (see procedure for carbon steels in the electrolytic method for nickel). Warm the ether extracted acid solution to expel residual ether, and oxidize with  $\text{KClO}_3$ . Dilute to 200 ml., and complete the determination as described in Section 1. In material containing very little cobalt, it is advantageous to combine the extracted acid solution obtained in ether separations of a number of separate 10-g samples.

**3. Cast Iron, Open-Hearth Iron, and Wrought Iron.**—Determine cobalt in accordance with the procedure described in Section 2.

### THE NITROSO-R-SALT (PHOTOMETRIC) METHOD (E30-60T) (FOR STAINLESS STEEL)

**Scope.**—This method covers a photometric procedure for the determination of cobalt in stainless steel, in the range of 0.01 to 0.30% cobalt.

**Summary of Method.**—Cobalt, in hot solution buffered with sodium acetate, forms an orange-colored complex with nitroso-R-salt. The addition of  $\text{HNO}_3$  destroys interfering complexes and stabilizes the cobalt complex. Photometric measurement is made at approximately 520  $\mu$ . Zinc oxide precipitation removes certain interfering elements, and eliminates the need for a correction for background color.

**Concentration Range.**—The recommended concentration range is from 0.005 to 0.15 mg. of cobalt in 50 ml. of solution, using a cell depth of 1 cm. (Note 20).

**NOTE 20.**—This procedure has been written for cells having a 1-cm. light path. Cells having a light path not exceeding 2 cm. may be used, provided the sample size is adjusted so that the amount of cobalt in the aliquot of the sample solution does not exceed 0.075 mg.

reactions may be made after solution of the residue and colorimetric determinations of the contaminants.

<sup>94</sup> Tests on a 0.5-g. sample of a steel containing 10% of cobalt and 6% of nickel showed but 0.1 mg. of nickel in the first precipitate.

**Stability of Color.**—The color is stable for at least 4 hr.

**Interferences.**—Iron, chromium, vanadium, nickel, manganese, and copper form complexes with nitroso-R-salt that deplete the reagent and inhibit the formation of the colored cobalt complex. Iron, chromium, and vanadium are removed from the solution by zinc oxide precipitation. A sufficient amount of nitroso-R-salt is used to provide full color development with 0.15 mg. of cobalt in the presence of 20 mg. of nickel, 6 mg. of manganese, and 1.25 mg. of copper. Colored complexes of nickel, manganese, and copper are destroyed by treating the hot solution with  $\text{HNO}_3$ .

**Reagents.** (a) **Cobalt, Standard Solution** (1 ml. = 0.06 mg. Co).—Transfer 0.3000 g. of high-purity cobalt (containing less than 0.3% nickel) to a 400-ml. tall-form beaker. Add 15 ml. of  $\text{HCl}$  (1:1), cover the beaker and heat until the cobalt is dissolved. Add 10 ml. of  $\text{HCl}$  and dilute the solution to about 150 ml. Neutralize the solution, using pH paper, by the dropwise addition of  $\text{NH}_4\text{OH}$ . Add 1 g. of hydroxylamine hydrochloride and stir well for 1 to 2 min. while the salt is dissolving. Add 5 ml. of  $\text{NH}_4\text{OH}$  in excess, and dilute to approximately 275 ml. with water. Electrolyze on a clean platinum electrode, starting with a current density of 3 amp. per sq. dm. until the color of the solution begins to turn from brown to pink and the cobalt starts to deposit. Continue the electrolysis with a current density of 1 amp. per sq. dm. until the deposition is nearly complete, as indicated by disappearance of the pink color. Alternatively, the entire electrolysis procedure may be conducted by controlling the cathode potential at  $-0.9$  v. with respect to a saturated calomel reference electrode, preferably with an automatic potentiostat. Rinse, dry, and weigh the electrode, and dissolve the cobalt from it using a sufficient amount of hot  $\text{HCl}$  (1:9) to cover the electrode. Rinse the electrode and collect the rinsings in the solution. Dry and reweigh the electrode. Dilute the solution to 500 ml. in a volumetric flask and mix. Calculate the exact concentration of cobalt in the solution on the basis of the amount of cobalt dissolved from the electrode. By means of a pipet, transfer 50.00 ml. of the solution to a 500-ml. volumetric flask, dilute to volume, and mix. (Note 21.)

NOTE 21.—If cells having a 2-cm. light path are used, dilute 50.00 ml. of the cobalt solution (1 ml. = 0.6 mg. Co) to 1 liter.

(b) **Zinc Oxide Suspension.**—Add finely-powdered  $\text{ZnO}$  to water in the ratio of 10 g. of  $\text{ZnO}$  to 60 ml. of water, and shake thoroughly. The suspension should be freshly prepared in an amount sufficient for one day's analyses.

(c) **Sodium Acetate Solution** (500 g. per liter).—Dissolve 500 g. of  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$  in about 600 ml. of water, filter and dilute to 1 liter.

(d) **Nitroso-R-Salt Solution** (7.5 g. per liter).—Dissolve 1.50 g. of nitroso-R-salt in water, filter, and dilute to 200 ml. Do not use solutions more than 1 week old.

**Preparation of Calibration Curve.** (a) **Calibration Solutions.**—By means of pipets, transfer 5, 10, 15, 20, and 25 ml. of cobalt solution (1 ml. = 0.06 mg. Co) to five 100-ml. volumetric flasks and dilute to volume with water. By means of a pipet, transfer 10 ml. of each solution to a 50-ml. volumetric flask. Proceed in accordance with Paragraph (c).

(b) **Reference Solution.**—Transfer 10 ml. of water to a 50-ml. volumetric flask and proceed in accordance with Paragraph (c).

(c) **Color Development.**—Add 5 ml. of sodium acetate solution followed by 5.00 ml. of nitroso-R-salt solution, swirling after each addition. Place the flask in boiling water to a depth of at least  $\frac{1}{2}$  in. After 6 to 10 min., add 5.0 ml. of  $\text{HNO}_3$



(1:2), and mix by swirling the flask. Continue the heating for 2 to 4 min., remove the flask from the boiling water, and then cool the solution to room temperature. Dilute to volume and mix.

(d) **Photometry.**—Transfer a suitable portion of each solution to an absorption cell and measure the transmittance or absorbance against the reference solution at 520  $m\mu$ .

(e) **Cell Correction.**—When two absorption cells are used, fill both cells with the reference solution and measure the transmittance or the absorbance at 520  $m\mu$  and record the cell correction.

(f) **Calibration Factor or Curve.**—Apply the cell correction and calculate the ratio of milligrams of cobalt to absorbance at each level of cobalt. If the ratios are constant, within experimental error, calculate the average value of the ratios to find the factor to apply to convert absorbance to milligrams of cobalt. If the ratios are not constant, or if for other reasons it is desirable, plot the absorbance or transmittance values against milligrams of cobalt per 50 ml. of solution.

**Procedure.** (a) **Test Solution:**

(1) Transfer 0.500 g. of the sample to a 100-ml. volumetric flask. (Note 20.) Add 5 ml. of a mixture of 1 volume of  $\text{HNO}_3$  and 3 volumes of  $\text{HCl}$ . Heat gently until the sample is dissolved and then boil the solution until brown fumes have been expelled. Add 65 to 70 ml. of water and cool.

(2) Add  $\text{ZnO}$  suspension in portions of about 5 ml. until the iron is precipitated and a slight excess of  $\text{ZnO}$  is present. Shake thoroughly after each addition of the precipitant and avoid a large excess. When sufficient  $\text{ZnO}$  has been added, further addition of the reagent causes the brown precipitate to appear lighter in color upon thorough shaking. A sufficient excess is indicated by a slightly white and milky supernatant liquid. Dilute the solution to volume and mix. Allow the precipitate to settle and filter a portion of the solution through a dry, fine paper into a clean, dry 250-ml. beaker. By means of a pipet, transfer 10 ml. of the filtrate to a 50-ml. volumetric flask and proceed as described in the section on preparation of calibration curve

(b) **Reference Solution.**—Transfer 10 ml. of water to a 50-ml. volumetric flask. Proceed as described in the section on preparation of the calibration curve.

(c) **Photometry.**—Take the photometric reading of the sample solution as described in the section on preparation of the calibration curve.

(d) **Cell Correction.**—Determine the cell correction in accordance with the section on preparation of the calibration curve.

**Calculation.**—Apply the cell correction and calculate the percentage of cobalt as follows (Note 22):

$$\text{Cobalt, per cent} = AF \times 2$$

where  $A$  = corrected absorbance, and

$F$  = factor, ratio of milligrams of cobalt to absorbance.

**NOTE 22.**—If a calibration curve is used, read the value for milligrams of cobalt from the curve. Substitute this value for  $AF$  in the equation.

## TITANIUM

## THE PHOTOMETRIC METHOD

**Reagents.** (a) Cupferron Solution (60 g. per liter).

(b) Standard Titanium Sulfate Solution (1 ml. = 0.0005 g. Ti).

**Procedure.** 1. *Titanium Steels.*—(a) Transfer 0.5 to 1 g. of the sample to a 400-ml. beaker, add 100 ml. of HCl (1:4), cover, and heat gently until action ceases. Cool the solution to 10° to 15°C., and add cupferron (60 g. per liter) drop by drop, while stirring constantly, until the precipitate just assumes a reddish-brown color. Additional cupferron only causes more iron to be precipitated. Add an ample quantity of ashless paper pulp and filter through an 11-cm. rapid paper. Wash 12 to 15 times with cold HCl (1:9).

(b) Transfer the paper and residue to a 50-ml. platinum crucible, dry, and ignite at a temperature (below 500°C.) just sufficient to destroy the carbon of the filter paper. Fuse the contents of the crucible with 1 g. of  $K_2S_2O_7$  (or a sufficient amount to give a clear fusion) at a temperature not over 750°C., and dissolve the cooled melt in 25 ml. of  $H_2SO_4$  (1:9).

(c) Transfer the cool solution to a 100-ml. volumetric flask, dilute to the mark with  $H_2SO_4$  (1:9), and mix thoroughly. Transfer a portion of the solution to a matched absorption cell and use this solution to set the 100% transmittancy point on a photoelectric photometer, using a blue filter (425 m $\mu$ ). Add 1 ml. of  $H_2O_2$  to the solution in the flask, mix thoroughly, and measure the percentage absorbance or transmittance at 425 m $\mu$ . Determine the percentage of titanium from a graph prepared from data obtained by carrying steels containing known amounts of titanium through all steps of the method.<sup>95</sup>

(d) If the steel contains an appreciable amount of copper, filter the solution of the sample (Paragraph (a)) through a small paper containing some paper pulp. Wash well with hot  $H_2SO_4$  (1:9). Cool the filtrate to 15° to 20°C. and precipitate with cupferron as described in Paragraph (a). Transfer the paper containing the acid-insoluble material to a 250-ml. beaker, add 25 ml. of  $HNO_3$  (3:7), and heat until the copper has dissolved. Add 50 ml. of hot water and a slight excess of  $NH_4OH$ . Heat to boiling, filter, and wash the paper and precipitate with hot water. Burn off the paper at as low a temperature as possible and add the residue to the ignited cupferron precipitate (Paragraph (b)). Fuse the combined residues with  $K_2S_2O_7$ , and dissolve in  $H_2SO_4$  (1:9). Determine titanium photometrically as described in Paragraph (c).

(e) If the steel contains vanadium (more especially when small amounts of titanium are sought), transfer the ignited cupferron precipitate (Paragraph (b)) to a 100-ml. platinum dish, add 5 ml. of HF and 10 ml. of  $HClO_4$ , and evaporate to a volume of 5 ml. or less. Cool somewhat, dilute to 50 ml., and add an excess of 5 ml. of NaOH (100 g. per liter). Boil for several minutes, let settle, and filter on a 9-cm. close-texture paper. Wash the paper and precipitate with hot water, ignite, fuse with a small amount of  $K_2S_2O_7$ , and complete the determination as described in Paragraph (c).

<sup>95</sup> As the presence of  $H_3PO_4$  affects the optical density of the titanium-peroxide color above 400 m $\mu$ , it is necessary, if  $H_3PO_4$  is added to the test solution, to have the same concentration of  $H_3PO_4$  in the solutions used to prepare the graph.

**2. Carbon Steels, Open-Hearth Iron, and Wrought Iron Containing Under 0.5% Titanium.**—Dissolve 5 g. of the sample in 150 ml. of HCl (1:4), and complete the determination as described in Section 1.

**3. Cast Iron.**—(a) Add 100 ml. of HCl (1:2) to 5 g. of the sample, cover, and warm. When all action has ceased, cool to 10° to 15°C., add 2 ml. of cupferron solution (60 g. per liter), and filter on a close-texture paper. Wash the insoluble matter 12 to 15 times with cold HCl (1:9).

(b) Transfer the paper and residue to a platinum crucible, dry, and ignite under good oxidizing conditions in an uncovered crucible until all carbon is gone. Add 1 to 2 ml. of HF and 1 ml. of H<sub>2</sub>SO<sub>4</sub> (1:5), and evaporate to dryness.

(c) Fuse the residue with 1 to 2 g. of Na<sub>2</sub>CO<sub>3</sub>. Dissolve the melt in about 50 ml. of water, digest for 15 min. at 90° to 95°C., filter, and wash with water. Ignite the residue in platinum, and fuse with 1 to 3 g. of K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>.

(d) Cool, dissolve the melt in 25 ml. of H<sub>2</sub>SO<sub>4</sub> (1:9), and complete the determination as described in Section 1, Paragraph (c).

## ZIRCONIUM

### THE CUPFERRON-PHOSPHATE METHOD

**Reagents.** Diammonium Phosphate Solution (120 g. per liter).

**Procedure.** **1. Zirconium Steels (Absence of Niobium and Tungsten).**—(a) Transfer 2 to 3 g. of the sample to a 250-ml. beaker. Add 100 ml. of HCl (1:4), cover, and heat until action ceases. Dilute to 150 ml., cool to 10° to 15°C., precipitate with cupferron, filter, and fuse the ignited precipitate with K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> as described for the determination of titanium. Dissolve the cooled melt in 100 ml. of H<sub>2</sub>SO<sub>4</sub> (1:9), and filter through a small paper to separate any siliceous matter that may be present. Wash with H<sub>2</sub>SO<sub>4</sub> (1:9).

(b) To the filtrate, add 2 ml. of H<sub>2</sub>O<sub>2</sub> and 25 ml. of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (120 g. per liter). Stir vigorously and let stand for 1 to 2 hr. at a temperature of 60° to 65°C. An excess of H<sub>2</sub>O<sub>2</sub> must be present at all times, and with amounts of zirconium under 0.01%, the solution should be allowed to stand at room temperature overnight. Filter through a 9-cm. paper containing ashless pulp, and wash thoroughly with cold NH<sub>4</sub>NO<sub>3</sub> (50 g. per liter).

(c) Transfer the paper and residue to a platinum crucible and ignite very carefully so that the paper chars but does not flame. When the paper has charred, gradually increase the temperature until all carbon is gone, and then heat at about 1050°C. for 15 min. Cool in a desiccator and weigh as ZrP<sub>2</sub>O<sub>7</sub>.

(d) In very accurate analysis, test the pyrophosphate for titanium by fusing with 4 to 5 g. of K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> and dissolving the melt in 40 ml. of H<sub>2</sub>SO<sub>4</sub> (1:9) containing 5 ml. of H<sub>2</sub>O<sub>2</sub> (3%). If titanium is present, determine it colorimetrically in accordance with the photometric method for titanium in steels, Paragraph (c), and calculate to Ti<sub>2</sub>P<sub>2</sub>O<sub>9</sub>.

(e) **Calculation.**—Calculate the percentage of zirconium as follows:

$$\text{Zirconium, per cent} = \frac{(A - B) \times 0.344}{C} \times 100$$

where *A* = grams of ZrP<sub>2</sub>O<sub>7</sub> (Paragraph (c)),

*B* = grams of Ti<sub>2</sub>P<sub>2</sub>O<sub>9</sub> (Paragraph (d)), and

*C* = grams of sample used.

**2. Carbon Steels, Open-Hearth Iron, Wrought Iron, and Cast Iron.**—Dissolve 5 g. of the sample in 150 ml. of HCl (1:4) and complete the determination as described in Section 1.

## ALUMINUM

### THE BICARBONATE-SODIUM HYDROXIDE METHOD (SMALL AMOUNTS OF ALUMINUM IN THE ABSENCE OF BERYLLIUM)

**Reagents.** (a) Hydrogen Sulfide Wash Solution.—Saturate HCl (1:99) with  $H_2S$ .

(b) Ammonium Thiocyanate Solution.—Dissolve 4 g. of  $NH_4CNS$  in 100 ml. of ethylene glycol monomethyl ether (methyl cellosolve).

(c) Ammonium Molybdate-Hydrazine Sulfate Solution.—Dissolve 0.15 g. of hydrazine sulfate in 100 ml. of water. Dissolve 1 g. of ammonium molybdate ( $(NH_4)_2MoO_4$ ) in 100 ml. of  $H_2SO_4$  (1:5). Dilute 10 ml. of the ammonium molybdate solution to 90 ml. with water, add 1 ml. of the hydrazine sulfate solution, and dilute the mixed solutions to 100 ml. with water. The ammonium molybdate-hydrazine sulfate solution is not stable and should be prepared as needed.

**Procedure.** **1. Carbon Steels Containing Under 0.1% Aluminum.**—(a) Transfer 10 g. of the sample to a 500-ml. Erlenmeyer flask and add exactly 110 ml. of  $H_2SO_4$  (1:9). Cover the flask with a small cover glass, and heat at  $80^\circ$  to  $90^\circ C$ . until action ceases. Dilute to a volume of 150 ml. with hot water, heat to boiling, and, while agitating the solution, add  $NaHCO_3$  (80 g. per liter) from a buret until a slight permanent precipitate forms (approximately 36 ml. in the usual case). Then add 5 ml. in excess.<sup>96</sup>

(b) Cover the flask, boil for 1 min., and allow the precipitate to settle. Filter through an 11-cm. rapid paper, and wash the flask and precipitate twice with warm water. The filtrate may become cloudy through hydrolysis of iron, but this is of no consequence.

(c) Return the paper and precipitate to the flask. Add 40 ml. of HCl (1:3), cover the flask, and heat moderately until the precipitate has dissolved. Agitate the flask until the paper is pulped, and then filter the solution through a 9-cm. close-texture paper into a 400-ml. beaker.<sup>97</sup> Wash the paper and residue 8 to 10 times with hot HCl (5:95) and then 3 to 4 times with hot water. Reserve the filtrate.

(d) Place the paper in a platinum crucible<sup>98</sup> and ignite under good oxidizing conditions and at a low temperature (not over  $500^\circ C$ .). Fuse the residue with 1 to 1.5 g. of  $K_2S_2O_7$ , and dissolve the cooled melt in the reserved filtrate (Paragraph (c)).<sup>99</sup>

<sup>96</sup> Chromium, copper, cobalt, nickel, niobium, phosphorus, tin, titanium, tantalum, uranium, vanadium, tungsten, zirconium, and ferric iron accompany the aluminum, some completely, others in part.

<sup>97</sup> The paper will contain aluminum oxide and aluminum silicate insoluble in  $H_2SO_4$  (1:9). Aluminum nitride is soluble in  $H_2SO_4$  (1:9). If acid-soluble aluminum only is wanted, this filtration can be omitted. In this case, dilute the solution to 200 ml., treat with  $H_2S$ , filter, and wash, as described in Paragraph (e) above.

<sup>98</sup> If the steel contains from 0.1 to 1% of elements such as copper or chromium, the paper and residue preferably should be ignited in porcelain at a low temperature (to prevent fusion with the glaze), and the ignited residue then transferred to a platinum crucible for the fusion.

<sup>99</sup> If a determination of acid-insoluble aluminum is desired, dissolve the melt in 20 ml. of HCl (1:3), dilute to 100 ml., treat with  $H_2S$ , filter, oxidize with  $HNO_3$ , treat with

(e) Dilute the solution to 200 ml. with hot water, and pass a brisk stream of  $H_2S$  through the solution as it cools to room temperature.<sup>100</sup> Filter the solution through a 9-cm. close-texture paper into a 400-ml. beaker. Wash the beaker and paper well with  $H_2S$  wash solution.

(f) Boil the filtrate until the  $H_2S$  is expelled. Add 2 ml. of  $HNO_3$  (or an amount sufficient for complete oxidation of the iron), and reduce the volume of the solution to about 75 ml. by boiling. Nearly neutralize the acid solution with  $NaOH$  (100 g. per liter) (about 50 to 60 ml. is usually required), heat to about  $70^\circ C.$ , and pour slowly into 120 ml. of hot  $NaOH$  (100 g. per liter), while stirring vigorously. Boil for 1 to 2 min., cool to room temperature, and filter through double 11-cm. close-texture papers,<sup>101</sup> catching the filtrate in a 600-ml. beaker. Wash the precipitate several times with  $NaOH$  (5 g. per liter).<sup>102</sup>

(g) Make the filtrate slightly acid with  $HCl$ , add 10 ml. of  $NH_4NO_3$  (500 g. per liter), and heat the solution just to boiling. Add a few drops of methyl red indicator, and carefully add  $NH_4OH$ , drop by drop, until the color of the solution changes to a distinct yellow. Boil the solution for 1 to 2 min., allow to digest until the precipitate has coagulated (usually 10 to 12 min.), and filter through a 9-cm. rapid paper. Wash the beaker and paper 3 or 4 times with hot, neutral  $NH_4NO_3$  (20 g. per liter).

(h) Return the paper and precipitate to the beaker, add 40 ml. of  $HCl$  (1:3), and digest until the precipitate has dissolved. Macerate the paper to a pulp. Dilute the solution to a volume of 125 to 150 ml., and repeat the precipitation with  $NH_4OH$  as previously described. Transfer the precipitate to the filter, and wash well with hot, neutral  $NH_4NO_3$  (20 g. per liter).

(i) Transfer the precipitate and paper to a weighed platinum crucible, and ignite until the carbon is gone. Cool, and treat the precipitate with a few drops of  $H_2SO_4$  (1:3) and 2 to 3 ml. of  $HF$ . Evaporate to dryness, and ignite to constant weight at  $1200^\circ C.$

(j) Examine the ignited oxides for  $Fe_2O_3$ ,  $P_2O_5$ ,  $Cr_2O_3$ , and  $V_2O_5$  in accordance with Paragraphs (k) to (o).

(k) Fuse the ignited oxides with 1 g. of  $K_2S_2O_7$ . Dissolve the melt in 20 ml. of  $HCl$  (1:1), dilute the solution to exactly 50 ml. with water, and mix thoroughly.

(l) Iron.—Transfer a 2-ml. aliquot of the solution (Paragraph (k)) to a test tube and add 8 ml. of ammonium thiocyanate solution. Compare the color developed with that of reference standards prepared in the same way.

(m) Phosphorus.—Transfer a 2-ml. aliquot of the solution (Paragraph (k)) to a 250-ml. beaker and add 30 ml. of ammonium molybdate-hydrazine sulfate solution. Heat on a steam bath for 15 to 20 min. (until the color is fully developed) and then cool the solution. Dilute to 50 ml. with ammonium molybdate-hydrazine sulfate solution, and compare the color with that of reference standards prepared in the same way.

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$NaOH$ , and complete the determination of aluminum as  $Al_2O_3$ , as describe in the method for total aluminum (Paragraphs (g) to (q)).

<sup>100</sup> Almost all steels contain small amounts of tin, which may be removed conveniently at this point.

<sup>101</sup> It is recommended that the paper first be washed two or three times with hot  $NaOH$  (20 g. per liter) and the washings discarded, in order to eliminate the possibility of extraction of organic matter by the solution.

<sup>102</sup> In work of high accuracy, the  $NaOH$  separation must be made in platinum (preferably), quartz, or Vycor-glass vessels. Alkaline solutions, especially when hot, extract silica and alumina from glass or porcelain vessels.

(n) **Chromium.**—Neutralize the remainder of the solution (Paragraph (k)) with NaOH (300 g. per liter), and then add 10 ml. in excess. Add a few milliliters of  $\text{H}_2\text{O}_2$  (3%), and boil until the chromium is oxidized. Cool, and compare the color with that of reference standards prepared in the same way.

(o) **Vanadium.**—Acidify the solution used for the determination of chromium with  $\text{H}_2\text{SO}_4$  (1:1), add a few milliliters of  $\text{H}_2\text{O}_2$  (3%), and compare the color with that of reference standards prepared in the same way.

(p) **Blank.**—Make a blank determination, following the same procedure and using the same amounts of all reagents.

(q) **Calculation.**—Calculate the percentage of aluminum as follows:

$$\text{Aluminum, per cent} = \frac{(A - B) \times 0.529}{C} \times 100$$

where  $A$  = grams of  $\text{Al}_2\text{O}_3$  from sample, corrected for  $\text{Fe}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{V}_2\text{O}_5$ ,  
 $B$  = grams of  $\text{Al}_2\text{O}_3$  from blank, corrected for  $\text{Fe}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{V}_2\text{O}_5$ , and  
 $C$  = grams of sample used.

## LEAD

### THE SULFIDE-MOLYBDATE METHOD

**Reagents.** (a) **Ammonium Molybdate Solution** (50 g. per liter).—Dissolve 10 g. of ammonium heptamolybdate  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 200 ml. of water by heating gently. If the solution is not clear, filter it. One milliliter will precipitate approximately 0.055 g. of lead.

(b) **Hydrogen Sulfide Wash Solution.**—Saturate HCl (1:99) with  $\text{H}_2\text{S}$ .

**Procedure.** 1. **Carbon Steels Containing Over 0.01% Lead.**—(a) Transfer 5 to 10 g. of the sample to a 600-ml. beaker and add 50 to 100 ml. of HCl (1:1). Cover the beaker and heat to hasten solution of the sample. When the sample has dissolved, evaporate the solution just to dryness in order to expel the excess acid,<sup>103</sup> but do not bake.<sup>104</sup> Add 400 ml. of hot water and heat, while stirring occasionally, until the iron salts have completely dissolved. Add 10 g. of  $\text{NH}_4\text{Cl}$ , and pass a rapid stream of  $\text{H}_2\text{S}$  through the solution for at least 10 min. Filter through a hardened paper,<sup>105</sup> and wash with cold  $\text{H}_2\text{S}$  wash solution.

(b) Dissolve the PbS in hot  $\text{HNO}_3$  (1:1),<sup>106</sup> catching the solution in a 250-ml. beaker, and wash the paper thoroughly with hot water. The filtrate and washings should not exceed 100 ml. Add 2 g. of tartaric acid. When the acid has dissolved, neutralize the solution with  $\text{NH}_4\text{OH}$  and add 5 ml. in excess for each 100 ml. of solution. Heat the ammoniacal solution to boiling, add 10 ml. of ammonium molybdate (50 g. per liter), and boil for a few minutes until the lead molybdate ( $\text{PbMoO}_4$ ) has coagulated. Filter through a close-texture paper containing some

<sup>103</sup> This step is important, as the pH of the solution when treated with  $\text{H}_2\text{S}$  has a decided influence on the completeness of the PbS precipitation. The proper pH for the precipitation is between 2.0 and 2.5, and the pH should be adjusted so that it falls within this range. Below a pH of 1.8 the PbS is not quantitatively precipitated, and above a pH of 3.0 iron accompanies the PbS.

<sup>104</sup> If the salts are baked, they are not completely soluble in hot water.

<sup>105</sup> Whatman 41H filter paper, or equivalent, is satisfactory for this purpose.

<sup>106</sup> Be sure that the PbS has completely dissolved and nothing but free sulfur remains on the paper. Usually about 10 ml. of the hot acid are sufficient to dissolve the PbS completely.

paper pulp and wash thoroughly with hot, slightly ammoniacal  $\text{NH}_4\text{NO}_3$  (50 g. per liter).

(c) Transfer the paper and precipitate to a weighed porcelain or quartz crucible, and ignite to constant weight in a muffle at  $600^\circ$  to  $650^\circ\text{C}$ . Cool in a desiccator, and weigh as  $\text{PbMoO}_4$ .

(d) Calculation.—Calculate the percentage of lead as follows:

$$\text{Lead, per cent} = \frac{A \times 0.564}{B} \times 100$$

where  $A$  = grams of  $\text{PbMoO}_4$ , and

$B$  = grams of sample used.

## NIOBIUM

### HYDROLYSIS WITH PERCHLORIC AND SULFUROUS ACIDS

**Reagents.** (a) Sulfurous Acid (6%).

(b) Sulfuric-Succinic Acid Solution.—Dissolve 5 g. of succinic acid in 500 ml. of  $\text{H}_2\text{SO}_4$  (1:4). Add a slight excess of  $\text{KMnO}_4$ .

(c) Ferric Phosphate Solution.—Dissolve 100 g. of  $\text{Fe}_2(\text{SO}_4)_3$  in 1 liter of water to which 150 ml. of  $\text{H}_3\text{PO}_4$  (85%) and 20 ml. of  $\text{H}_2\text{SO}_4$  (1:1) have been added. Add  $\text{KMnO}_4$  (25 g. per liter) until the solution is just tinted pink, due to the excess of  $\text{KMnO}_4$ .

(d) Standard Potassium Permanganate Solution (0.05  $N$ ).

(e) Ammonium Chloride Wash Solution.—Dissolve 20 g. of  $\text{NH}_4\text{Cl}$  in water, add 1 ml. of  $\text{NH}_4\text{OH}$ , and dilute to 1 liter.

**Procedure. 1. Niobium Steels (Tungsten Absent).—**(a) Transfer 2.5 g. of the sample to a 400-ml. beaker, add 25 ml. of  $\text{HCl}$  and 5 ml. of  $\text{HNO}_3$ , cover the beaker, and heat gently until action ceases and only carbides of niobium and other elements remain undissolved. Add 30 ml. of  $\text{HClO}_4$  and evaporate to white fumes. Cover the beaker and continue the boiling for at least 10 min., heating in such a manner that  $\text{HClO}_4$  refluxes on the sides of the beaker. Cool somewhat; then add 175 ml. of water, 50 ml. of  $\text{H}_2\text{SO}_3$ , and some ashless paper pulp. Boil the solution for 10 min. to hydrolyze niobium, and then digest at  $65^\circ$  to  $70^\circ\text{C}$ . for about 15 min. Filter the solution through an 11-cm. close-texture paper containing ashless paper pulp. Wash the beaker with  $\text{HCl}$  (1:49) and scrub it with a filter paper moistened with  $\text{HCl}$  (1:49). Add the paper to the filter and wash the residue and papers with  $\text{HCl}$  (1:49) until free of  $\text{HClO}_4$  (12 to 15 washings).

(b) Transfer the precipitate and papers to a 50-ml. platinum crucible or a 50-ml. platinum dish, char the paper, and ignite at a dull red heat. The residue consists of niobic and tantallic oxides contaminated by  $\text{SiO}_2$  and other oxides.

(c) To the residue in the platinum crucible (Paragraph (b)), add 3 to 5 ml. of  $\text{HF}$ , 2 ml. of  $\text{HClO}_4$ , and 6 ml. of  $\text{H}_2\text{SO}_4$  (1:1). Evaporate to dense white fumes and continue heating until the volume of the solution is reduced to about 2.5 ml. Hydrofluoric acid must be completely expelled, as it prevents hydrolysis of niobium in the subsequent precipitation. If any niobic acid separates, add 1 ml. of  $\text{H}_2\text{SO}_4$  and continue the heating for 1 to 2 min. Cool the crucible somewhat, and transfer the contents to a 400-ml. beaker by means of 200 ml. of hot  $\text{HCl}$  (1:49). Scrub the crucible with a filter paper moistened with  $\text{HCl}$  (1:49), and add the paper to the solution.

(d) To the solution (Paragraph (c)), add 50 ml. of  $\text{H}_2\text{SO}_3$ . Boil the solution for 10 min., add ashless paper pulp, and warm the solution at  $65^\circ$  to  $70^\circ\text{C}$ . for about 15 min., or until the supernatant liquid is clear. Filter through a close-texture paper containing paper pulp. Wash thoroughly with  $\text{HCl}$  (1:49).

(e) Place the paper in a 30-ml. platinum crucible or a 50-ml. platinum dish and char the paper at a low heat. Then ignite, preferably in a muffle furnace, at  $1000^\circ$  to  $1050^\circ\text{C}$ . to constant weight (usually about 15 min.). Cool in a desiccator and weigh as  $\text{Nb}_2\text{O}_5$ . The weighed residue will contain any tantalum and most of the tungsten present in the steel.<sup>107</sup>

(f) **Calculation.**—Calculate the percentage of niobium as follows:

$$\text{Niobium, per cent} = \frac{A \times 0.699}{B} \times 100$$

where  $A$  = grams of  $\text{Nb}_2\text{O}_5$ , and  
 $B$  = grams of sample used.

**Niobium by Titration with Potassium Permanganate (Tantalum by Difference).**—(g) If desired, the actual niobium content can be determined by reduction in a Jones reductor followed by titration with 0.05  $N$   $\text{KMnO}_4$ , as described in Paragraphs (h) to (l).

(h) Add 0.0500 g. of  $\text{TiO}_2$  and 3 g. of  $\text{K}_2\text{S}_2\text{O}_7$  to the oxides in the platinum crucible. Heat moderately until the oxides are dissolved. Cool the melt and add 5 ml. of  $\text{H}_2\text{SO}_4$ . Heat until the melt is dissolved. Transfer the solution to a 250-ml. beaker, and rinse the crucible with three 5-ml. portions of  $\text{H}_2\text{SO}_4$ . Then rinse the crucible with 20 ml. of the sulfuric-succinic acid solution. Stir the solution and dilute to 100 ml. Add  $\text{KMnO}_4$  to a distinct pink color. The solution is now ready for passing through the Jones reductor.

(i) If the reductor has been standing idle, pass 100 ml. of warm ( $40^\circ$  to  $50^\circ\text{C}$ .)  $\text{H}_2\text{SO}_4$  (5:95) through it and then some water, and discard the wash solution. Place 25 ml. of the ferric phosphate solution in a 1-liter suction flask, and connect the flask and reductor so that the tip of the reductor is immersed in the solution. Open the stopcock and, without allowing the zinc at the top of the reductor to become dry at any time, pass through the reductor in succession 150 ml. of the warm ( $70^\circ\text{C}$ .) sulfuric-succinic acid solution, the warm ( $60^\circ\text{C}$ .) solution of niobium, 100 ml. of warm sulfuric-succinic acid solution, and three 50-ml. portions of hot water, closing the stopcock with the water just covering the top of the zinc.

(j) Cool the flask and solution in ice water or by adding ice cubes made from distilled water. Transfer the solution to an 800-ml. beaker, add 2 drops of 1,10-phenanthroline-ferrous sulfate indicator, and titrate with 0.05  $N$   $\text{KMnO}_4$  to the disappearance of the red color.

(k) **Blank.**—Make a blank determination by fusing 0.0500 g. of  $\text{TiO}_2$  with 3 g. of  $\text{K}_2\text{S}_2\text{O}_7$ , dissolving the melt in the sulfuric-succinic acid solution, passing the solution through the reductor, and following exactly the same procedure as used for the analysis.

<sup>107</sup> Small amounts of platinum may be found occasionally in the final ignited oxides. In very accurate work the oxides should be examined for platinum, which, if found, should be determined and deducted. The ignited residue may also contain small amounts of tungsten and phosphorus. If the tungsten content is suspected or known to be over 0.05%, the procedure described in the section on Tungsten Steels, Paragraphs (a) to (d) shall be followed for results of the highest accuracy.



(1) **Calculation.**—Calculate the percentages of niobium and tantalum as follows:

$$\text{Niobium, per cent} = \frac{(A - B)C \times 0.0465}{D} \times 100$$

$$\text{Tantalum, per cent} = \frac{(E - 1.43F) \times 0.819}{D} \times 100$$

where  $A$  = milliliters of  $\text{KMnO}_4$  solution required for titration of the sample,  
 $B$  = milliliters of  $\text{KMnO}_4$  solution required for titration of the blank,  
 $C$  = normality of the  $\text{KMnO}_4$  solution,  
 $D$  = grams of sample used,  
 $E$  = grams of mixed oxides (Paragraph (e)), and  
 $F$  = grams of niobium determined as described in Paragraphs (g) to (k).

**2. Molybdenum and Titanium Steels.**—(a) Determine niobium in accordance with the procedure described in Section 1 (a) to (e). If the steel contains more than 0.5% of molybdenum or 0.1% of titanium, the final hydrolysis precipitate will contain small amounts (about 0.1 to 0.02%) of each of these elements. The niobium (plus tantalum) value indicated by the weight of the ignited oxides (see Section 1 (e)) can be corrected for these elements as described in the following Paragraphs (b) and (c).

(b) Dissolve the ignited oxides in 3 to 5 ml. of HF, add 10 ml. of  $\text{H}_2\text{SO}_4$  (1:1), and evaporate to white fumes to expel all HF. Cool to about 15°C., cautiously add 20 to 25 ml. of  $\text{H}_2\text{O}_2$  (3%), cool, and compare the yellow color with a titanium standard similarly prepared.<sup>108</sup>

(c) Add NaCNS and  $\text{SnCl}_2$ , extract the colored compound (preferably with butyl acetate), and compare with a molybdenum standard similarly treated.

(d) Calculate the weights of molybdenum and titanium to  $\text{MoO}_3$  and  $\text{TiO}_2$  and correct the weight of  $\text{Nb}_2\text{O}_5$  accordingly. Calculate the percentage of niobium as described in Section 1 (f).

**3. Tungsten Steels.**—(a) Dissolve the sample and precipitate niobium as described in Section 1 (a). Tungsten will also accompany niobium and shall be removed as described in Paragraphs (b) to (d).

(b) Ignite the precipitate in a platinum dish. Transfer the ignited precipitate to the original 400-ml. beaker, add 20 ml. of NaOH (100 g. per liter), cover, and heat to boiling for about 3 min. Dilute to 100 ml. with water, add an excess of HCl, and heat to boiling to dissolve any iron present. Add an excess of about 1 ml. of  $\text{NH}_4\text{OH}$ , and heat until only a faint odor of ammonia persists. Filter on a 9-cm. paper containing a little ashless paper pulp, and wash 18 to 20 times with hot  $\text{NH}_4\text{Cl}$  wash solution.

(c) Ignite in a 50-ml. platinum dish at a low temperature, cool, and add 3 to 5 ml. of HF, 2 ml. of  $\text{HClO}_4$ , and 6 ml. of  $\text{H}_2\text{SO}_4$  (1:1). Evaporate to dense white fumes, and continue the heating until the volume has been reduced to about 2.5 ml. Cool, cautiously add approximately 5 ml. of cold water, and transfer to a 400 ml. beaker containing an excess (about 50 ml.) of  $\text{NH}_4\text{OH}$  (1:4). Rinse the dish well with HCl (1:49). Scrub the dish with a filter paper moistened with HCl

<sup>108</sup> Niobium gives a very slight color with  $\text{H}_2\text{O}_2$  in  $\text{H}_2\text{SO}_4$  (1:9), equivalent in terms of titanium to about 0.2% of the niobium; for example, with 1% niobium, 0.002 should be subtracted from the indicated titanium ( $1.0 \times 0.002$ ).

(1:49) and add the paper to the solution. Should the solution become acid during the rinsing of the dish with HCl (1:49), add bromcresol purple as indicator, and then carefully add  $\text{NH}_4\text{OH}$  until the solution just becomes purple. Boil 1 min., or until only a faint odor of ammonia persists, filter on a 9-cm. close-texture paper, and wash the filter and precipitate 12 to 15 times with hot  $\text{NH}_4\text{Cl}$  wash solution.

(d) Transfer the paper and precipitate to the 400-ml. beaker, add 100 ml. of HCl (5:95) and 20 ml. of  $\text{H}_2\text{SO}_3$ , and boil the solution for 3 to 5 min. Digest at  $65^\circ$  to  $70^\circ\text{C}$ . for about 15 min., or until the precipitate has settled. Filter through a close-texture paper containing paper pulp, wash thoroughly with HCl (1:49), and complete the determination in accordance with Section 1' (e) to (l).

## NIOBIMUM AND TANTALUM

### THE HYDROLYSIS (PHOTOMETRIC) METHOD (E30-60T)

**Principle of Method.**—Niobium and tantalum are separated by double hydrolysis. The final mixed oxides also contain tungsten and titanium. Tantalum is determined photometrically by measurement of the color produced with pyrogalllic acid. Niobium and tungsten are determined by double photometry by measurement of the color produced with hydroquinone at two different wavelengths.

**Concentration Range.**—The recommended concentration ranges are 0 to 4 mg. of tantalum per 100 ml. and 0.0 to 0.4 mg. of niobium per 100 ml., using a cell depth of 1 cm. Other cell depths may be used by making suitable adjustments in the sample size.

**Stability of Colors.**—The stability of the colored complexes of tantalum, niobium, and tungsten is quite satisfactory. However, there is a very slow increase in the color densities due to intensification of the basic colors of the color-developing reagents themselves. Consequently, the reagents should be prepared just before use. Careful control of time and temperature are essential.

**Interfering Elements.**—(a) In addition to niobium and tantalum, the hydrolysis residue contains nearly all of the tungsten (if the tungsten is not in excess of that which can be carried down by the niobium and tantalum), and a small but significant amount of any titanium present. The presence of these elements necessitates the application of corrections as indicated in Paragraphs (b) and (c).

(b) **Corrections Required for Tantalum.**—The total absorbance reading at  $430\text{ m}\mu$  includes that due to tantalum plus absorbances due to titanium, niobium, and tungsten. The interference effect of these elements may be expressed as follows:

0.1 mg. Ti (0.01% Ti on 1-g. aliquot) = approximately 0.02 to 0.03% Ta

10 mg. Nb (1% Nb on 1-g. aliquot) = approximately 0.01% Ta

1 mg. W (0.1% on 1-g. aliquot) = approximately 0.005% Ta

The titanium interference is very significant and, therefore, correction must be made on all determinations. The interferences of niobium and tungsten are very small, but corrections should be made in analyses requiring the highest accuracy.

(c) **Corrections Required for Niobium and Tungsten.**—The total absorbance readings at 400 and  $520\text{ m}\mu$  include those due to niobium and tungsten plus absorbances due to titanium at 400 and  $520\text{ m}\mu$  and to tantalum at  $400\text{ m}\mu$ . The interference effect of these elements may be expressed as follows:

(1) At 400  $m\mu$ :

0.01 mg. Ti (0.025% Ti on 0.04-g. aliquot) = approximately 7 absorbance units

0.1 mg. Ta (0.25% Ta on 0.04-g. aliquot) = approximately 10 absorbance units

(2) At 520  $m\mu$ :

0.01 mg. Ti (0.025% Ti on 0.04-g. aliquot) = approximately 10 absorbance units

These corrections are quite small but should not be ignored in analyses requiring the highest accuracy.

**Reagents.** (a) **Ammonium Oxalate Solution** (40 g. per liter).—To 80.0 g. of ammonium oxalate add approximately 1 liter of water and heat until dissolved. Transfer the hot solution to a 2000-ml. volumetric flask and immediately dilute nearly to the mark with cold water. Cool to room temperature, dilute to the mark, and mix.

(b) **Pyrogalllic Acid Solution** (500 g. per liter).—Each determination requires 20 ml. Prepare the amount required (just prior to use, since this solution gradually becomes colored) in a glass-stoppered Erlenmeyer flask in the ratio of 50.0 g. of pyrogalllic acid to 100 ml. of water. Swirl occasionally until dissolved. The time required for dissolution is about 1 hr.

(c) **Hydroquinone-Sulfuric Acid Solution** (60 g. per liter).—Each determination requires 100 ml. Prepare the amount required (just prior to use, since this solution gradually becomes colored) in the ratio of 6 g. of hydroquinone per 100 ml. of  $H_2SO_4$ . Stir occasionally until dissolved. The time required for dissolution is about 1 hr.

(d) **Stannous Chloride Solution** (300 g. per liter).—Dissolve 30 g. of  $SnCl_2 \cdot 2H_2O$  in 100 ml. of HCl (1:1) by heating in a covered beaker. Cool and store in a glass-stoppered bottle.

(e) **Standard Tungsten Solution** (1 ml. = 0.1 mg. W).—Dissolve 0.0897 g. of  $Na_2WO_4 \cdot 2H_2O$  in water and dilute to 500 ml.

(f) **Standard Titanium Solution** (1 ml. = 0.15 mg. Ti).—Fuse 0.125 g. of  $TiO_2$  (less than 0.01% Ta or Nb) in a platinum crucible with 4 to 6 g. of  $KHSO_4$  or  $NaHSO_4$ . Leach in 100 ml. of  $H_2SO_4$  (1:1), dilute to about 200 ml., filter, and dilute to 500 ml. with water. Standardize as follows: transfer 50-ml. aliquots to each of two 250-ml. beakers, add 15 ml. of  $H_2SO_4$  (1:1), and cool to 5° to 10°C.; precipitate the titanium with 15 ml. of cupferron (aqueous solution (60 g. per liter)); add paper pulp, filter, and wash with cold water 8 to 10 times; ignite and weigh as  $TiO_2$ . Calculate the titanium equivalent of the solution, in milligrams per milliliter, as follows:

$$\text{Titanium equivalent} = \frac{A \times 0.5995}{50} \times 1000$$

where  $A$  = grams of  $TiO_2$ .

(g) **Standard Titanium Solution** (1 ml. = 0.015 mg. Ti).—Dilute 10 ml. of titanium solution (1 ml. = 0.15 mg. Ti) to 100 ml. in a volumetric flask.

(h) **Standard Tantalum Solution** (1 ml. = 0.25 mg. Ta).—Add 10 to 15 drops of  $H_2SO_4$  (1:1) to 0.272 g. of  $K_2TaF_7$  (less than 0.01% Ti or Nb) contained in a platinum crucible and evaporate to dryness under a hot plate or on a sand bath. Add 4 to 6 g. of  $KHSO_4$  or  $NaHSO_4$  and fuse at a low temperature until clear; heat

= 0.8 mg. Nb) to 100-ml. volumetric flasks. Proceed as directed in Paragraph (a) (1) and (2) for the determination of tantalum.

(2) Plot the absorbance readings against milligrams of niobium per 100 ml. From the known amount of niobium present in the sample (as determined in the Procedure), the absorbance correction to be applied to the tantalum reading can then be determined.

**(c) Correction of Tantalum Absorbance for Tungsten Present:**

(1) Transfer 5.0, 10.0, 15.0, and 25.0-ml. portions of the tungsten solution (1 ml. = 0.1 mg. W) to 100-ml. volumetric flasks. Proceed as directed in Paragraph (a) (1) and (2) for the determination of tantalum.

(2) Plot the absorbance readings against milligrams of tungsten per 100 ml. From the known amount of tungsten present in the sample (as determined in the Procedure), the absorbance correction to be applied to the tantalum reading can then be determined.

**(d) Correction of Tantalum Absorbance for Titanium Present:**

(1) Transfer 1.0, 2.0, 4.0, and 6.0-ml. portions of the titanium solution (1 ml. = 0.15 mg. Ti) to 100-ml. volumetric flasks. Proceed as directed in Paragraph (a) (1) and (2) for the determination of tantalum.

(2) Plot the absorbance readings against milligrams of titanium per 100 ml. From the known amount of titanium present in the sample (as determined under Tantalum Determination below), the absorbance correction to be applied to the tantalum reading can then be determined.

**Preparation of Correction Curves for Niobium and Tungsten. (a) Correction of Niobium Plus Tungsten Absorbances for Ti Present:**

(1) Transfer 1.0, 2.0, 4.0, and 6.0-ml. portions of the titanium solution (1 ml. = 0.015 mg. Ti) to 125-ml. Phillips beakers. Proceed as directed under Niobium Determination below for the determination of niobium and tungsten.

(2) Plot the absorbances at 400  $m\mu$  and 520  $m\mu$  against mg. titanium per 100 ml. From the known amount of titanium present in the sample (as determined in Paragraph (d) of the procedure), the absorbance corrections to be applied to the niobium plus tungsten readings at each wavelength can then be determined.

**(b) Correction of Niobium Plus Tungsten Absorbance at 400  $m\mu$  for Tantalum Present:**

(1) Transfer 1.0, 2.0, 3.0, 4.0, and 5.0-ml. portions of the tantalum solution (1 ml. = 0.025 mg. Ta) to 125-ml. Phillips beakers. Proceed as directed in the procedure for the determination of niobium and tungsten, obtaining absorbance readings at 400  $m\mu$  only.

(2) Plot the absorbances at 400  $m\mu$  only (tantalum shows no absorption at 520  $m\mu$ ) against mg. tantalum per 100 ml. From the known amount of tantalum present in the sample (as determined in the following Section), the absorbance correction to be applied to the niobium plus tungsten reading at 400  $m\mu$  can then be determined.

**Separation of Niobium and Tantalum by Hydrolysis.**—(a) Transfer 2.0 g. of sample to a 400-ml. beaker. If the niobium content is less than 0.20% (or if the tantalum content is less than 0.05%), use a 4.0-g. sample and increase the acid additions in proportion. Add 20 ml. of HCl and 5 ml. of HNO<sub>3</sub>, cover the beaker, and heat until action ceases and only carbides of niobium and other elements remain undissolved. Add 25 ml. of HClO<sub>4</sub> and evaporate to fumes. Cover the beaker and continue the fuming for at least 5 min. after the chromium is oxidized, heating in such a manner that the HClO<sub>4</sub> refluxes on the sides of the beaker. Cool somewhat,

add 175 ml. of hot water and 50 ml. of saturated  $\text{H}_2\text{SO}_3$  solution. Place a small piece of hardened filtered paper under the end of the stirring rod to prevent bumping and boil for 5 min. to hydrolyze the niobium, tantalum, and tungsten. Stir in a small amount of ashless paper pulp and digest at  $60^\circ$  to  $70^\circ\text{C}$ . for at least 30 min. (preferably 4 hr. or more). Filter through a medium paper containing a little paper pulp. Wash the beaker with hot  $\text{HCl}$  (2:98) and scrub it with a piece of hardened paper moistened with  $\text{HCl}$  (2:98). Add the paper to the filter, wash the beaker once more, and then wash the precipitate and paper with hot  $\text{HCl}$  (2:98) until free from perchlorates (about 10 to 12 washings).

(b) Transfer the precipitate and paper to a 30- or 40-ml. platinum crucible, char the paper, ignite at  $1000^\circ\text{C}$ . or higher for 10 min., and allow to cool. The residue consists of the oxides of niobium, tantalum, tungsten, titanium, and silicon plus small amounts of other oxides.

(c) Moisten the residue in the crucible with  $\text{H}_2\text{SO}_4$  (1:1) and add 3 to 5 ml. of  $\text{HF}$ . Evaporate cautiously to dryness, add 3 to 5 g. of  $\text{KHSO}_4$  or  $\text{NaHSO}_4$  and fuse at a low temperature until clear and then at a dull red heat for 1 min. Leach the fusion by heating in 100 ml. of  $\text{HCl}$  (2:98) in a 400-ml. beaker, and rinse and remove the crucible.

(d) Dilute to 200 ml. with hot  $\text{HCl}$  (2:98), add 40 ml. of saturated  $\text{H}_2\text{SO}_3$  solution, boil for 5 min., add some ashless paper pulp, and digest at  $60^\circ$  to  $70^\circ\text{C}$ . for at least 30 min. (preferably 4 hr. or more). Filter and wash as directed for the first precipitation.

(e) Transfer the paper and precipitate to a platinum crucible, char at a low heat, and then ignite at  $1000^\circ\text{C}$ . or higher for 10 min.

(f) Cool, add 3 to 5 g. of  $\text{KHSO}_4$  or  $\text{NaHSO}_4$ , and fuse at a low temperature until clear and then at a dull red heat for 1 min. (A blank consisting of 3 to 5 g. of  $\text{KHSO}_4$  or  $\text{NaHSO}_4$  should be started at this point, fused in platinum, and treated in the same manner as the sample.) Cool nearly to room temperature, add 5 drops of  $\text{H}_2\text{SO}_4$ , and again heat at a temperature just high enough to obtain a clear melt. Do not heat longer than is necessary lest an excessive amount of  $\text{H}_2\text{SO}_4$  be volatilized. Cool the fusion, leach in 50 ml. of ammonium oxalate by heating gently in a covered 250-ml. beaker. Remove the crucible and rinse with a small amount of water. Cool, transfer to a 100-ml. volumetric flask, dilute to the mark with the oxalate solution, mix thoroughly and reserve (Solution "A").

**Determination of Tantalum.**—(a) Transfer 50 ml. (representing 1.0 g. of sample) of Solution "A" to a 100-ml. volumetric flask. Add 10 ml. of  $\text{H}_3\text{PO}_4$  (1:3) and dilute to 60 to 75 ml. with oxalate solution. Add 20 ml. of freshly prepared pyrogalllic acid solution, mix, dilute to the mark with oxalate solution, and mix thoroughly. Allow to stand for 10 to 15 min. for complete color development. During this period adjust the temperature to within  $\pm 1^\circ\text{C}$ . of that temperature at which the calibration curve was established (a temperature close to the average room temperature is recommended).

(b) Add a portion of the blank solution to a 1-cm. cell and adjust the spectrophotometer to zero absorbance at  $430\text{ m}\mu$ . Measure the absorbance of the sample and record as:

Tantalum absorbance (uncorrected)

(c) The tantalum absorbance must be corrected for the absorbances due to niobium, tungsten, and titanium as follows:

$$\text{Tantalum absorbance (corrected)} = A - (B + C + D)$$

where  $A$  = total absorbance from curve,

$B$  = niobium absorbance at 430  $m\mu$ ,

$C$  = tungsten absorbance at 430  $m\mu$ , and

$D$  = titanium absorbance at 430  $m\mu$ .

The absorbance corrections to be applied are based on the milligrams of niobium, tungsten, and titanium present in the 50-ml. aliquot (equivalent to 1 g. of sample) used for the tantalum determination. These are determined as directed in the following sections.

(d) The milligrams of niobium and tungsten present are determined as directed in the next two sections. Since a 2-ml. (or 5-ml.) aliquot is used for the niobium and tungsten determinations, the milligrams of niobium and tungsten found are multiplied by 25 (or 10) to obtain the milligrams per 50 ml. Then, by reference to the correction curves for niobium and tungsten (Paragraphs (b) and (c) of Calibration and Correction Curves) the absorbance corrections to be applied to the tantalum reading may be determined.

(e) The milligrams of titanium present is determined as follows: transfer a 20-ml. aliquot of Solution "A" to a 25-ml. volumetric flask; add 1 ml. of  $H_2SO_4$  (1:1), 1 ml. of  $H_2O_2$  (30%); dilute to the mark, and mix; adjust the photometer to read zero absorbance at 430  $m\mu$  against water; and then measure the absorbance of the unknown solution; determine the amount of titanium present from a previously prepared calibration curve. Then:

$$\text{Titanium, mg. per 50 ml.} = \text{titanium found, mg.} \times \frac{50}{20}$$

By reference to the titanium correction curve (Paragraph (d)) the absorbance correction to be applied to the tantalum reading can be determined.

(f) From the corrected absorbance for tantalum as determined in Paragraph (c), the milligrams of tantalum present can be obtained by reference to the tantalum calibration curve (Paragraph (a)). Then,

$$\text{Tantalum, per cent} = \frac{A}{1000} \times \frac{100}{B} \times \frac{100}{C}$$

where  $A$  = milligrams of tantalum,

$B$  = weight of original sample, and

$C$  = milliliters in aliquot.

For a 2-g. sample diluted to 100 ml. and a 50-ml. aliquot taken:

$$\text{Tantalum, per cent} = \frac{A}{1000} \times \frac{100}{2} \times \frac{100}{50} = \frac{A}{10}$$

**Determination of Niobium (and Tungsten).**—(a) With an original sample size of 2.0 g. use a 2-ml. aliquot of Solution "A" for niobium, contents over 0.5% for less than 0.5% niobium use a 5-ml. aliquot. Transfer to a 125-ml. Phillips beaker. Also start a blank at this point consisting of 2 ml. (or 5 ml.) of the blank solution prepared in accordance with Paragraph (f) of the hydrolysis separation of niobium and tantalum. To sample and blank, add 10 ml. of  $H_2SO_4$  and 1 ml. of  $H_3PO_4$  (1:3), evaporate to dense white fumes, and fume gently for 10 min. Cool the flask

and contents to room temperature. Add 1 drop only of  $\text{SnCl}_2$  solution to reduce the iron and molybdenum, and mix immediately and thoroughly. Add approximately 50 ml. of the hydroquinone solution and mix thoroughly. Transfer to a dry 100-ml. volumetric flask and rinse out the Phillips beaker 3 to 4 times with approximately 10-ml. portions of the hydroquinone solution, adding each washing to the volumetric flask. Dilute to the mark with the hydroquinone solution and mix thoroughly. Allow to stand for 10 to 15 min. for complete color development. During this period adjust the temperature to within  $\pm 1^\circ\text{C}$ . of that temperature that was selected for calibration.

(b) Using 1 cm. cells, adjust the spectrophotometer to zero absorbance at 400  $m\mu$  with the blank solution. Measure the absorbance of the sample solution at 400  $m\mu$ . Adjust to zero absorbance at 520  $m\mu$  with the blank solution. Measure the absorbance of the sample solution at 520  $m\mu$ .

Repeat this sequence of operations for each sample.

(c) The total absorbance values at each wavelength must be corrected for the absorbance due to titanium. In addition, the total absorbance value at 400  $m\mu$  must be corrected for the absorbance due to tantalum. There is no correction for absorbance due to tantalum at 520  $m\mu$ . The absorbance corrections to be applied are based on the milligrams of titanium and tantalum present in the 2-ml. (or 5-ml.) aliquot used for the niobium and tungsten determination. Determine the absorbance corrections in accordance with the following Paragraphs (d) and (e).

(d) Calculate the milligrams of titanium per 2 ml. (or 5 ml.) as follows:

$$\text{mg. Ti/2 ml. (or 5 ml.)} = \frac{\text{mg. Ti/20 ml. (preceding section (c))}}{10 \text{ (or 4)}}$$

By reference to Paragraph (a) of the titanium correction curve, the corrections to be applied to the total absorbance readings at 400 and 520  $m\mu$  may be determined.

(e) Calculate the milligrams of tantalum per 2 ml. (or 5 ml.) as follows:

$$\text{mg. Ta/2 ml. (or 5 ml.)} = \frac{\text{mg. Ta/50 ml. preceding section (f))}}{25 \text{ (or 10)}}$$

By reference to Paragraph (b) of the tantalum correction curve, the correction to be applied to the total absorbance at 400  $m\mu$  may be determined.

(f) Calculate the corrected absorbance readings at 400 and 520  $m\mu$  from the following equations:

$$\text{Corrected absorbance at 400 } m\mu = A - (B + C)$$

$$\text{Corrected absorbance at 520 } m\mu = D - E$$

where  $A$  = total absorbance at 400  $m\mu$ ,

$B$  = absorbance due to titanium at 400  $m\mu$  (Paragraph (a) of correction curves),

$C$  = absorbance due to tantalum at 400  $m\mu$  (Paragraph (b) of correction curves),

$D$  = total absorbance at 520  $m\mu$ , and

$E$  = absorbance due to titanium at 520  $m\mu$  (Paragraph (a) of correction curves).

From the corrected absorbance readings, determine the milligrams of niobium and tungsten present by use of the formulas derived in the next section.

Calculations.—(a) Determine the slopes for 1 mg. of niobium at 400 and at 520  $m\mu$  as directed below and express in terms of absorbance  $\times 1000$ .

For a 2-g. sample diluted to 100 ml. and a 2-ml. aliquot taken:

$$\text{Niobium, per cent} = \frac{A}{1000} \times \frac{100}{2} \times \frac{100}{2} = A \times \frac{5}{2}$$

(g) The following order of calculations is recommended: Correct the absorbance readings for tantalum at 430 m $\mu$ , and for niobium and tungsten at 400 and 520 m $\mu$ , for the absorbances due to titanium. Calculate the per cent of niobium and tungsten (preliminary values). Based on these preliminary values, make the remaining corrections of the tantalum absorbance for the absorbances due to niobium and tungsten. Calculate the tantalum value (final). Based on the final tantalum value, correct the niobium and tungsten absorbance at 400 m $\mu$ . Calculate the niobium value (final).

## NITROGEN

### THE DISTILLATION-TITRATION METHOD

**Apparatus.**—The apparatus recommended for the determination of nitrogen by direct distillation is shown in Fig. 24-10. The apparatus consists essentially of a dropping funnel for introducing reagents, an 800-ml. long-neck Kjeldahl flask, a condenser, and a modified Volhard nitrogen receiving flask. The apparatus recommended for the determination of nitrogen by distillation with steam is shown in Fig. 24-11. The apparatus is essentially the same as that shown in Fig. 24-10, with the addition of suitable means of passing steam through the solution in the Kjeldahl flask.

**Reagents.** (a) **Selenium.**—Powdered selenium.

(b) **Low-Ammonia Water.**—Nearly fill a 12-l. flask with distilled water. Then add 4 g. of NaOH pellets and 2 g. of Devarda's alloy or 2 g. of a zinc-copper couple made by rolling together 15 sq. cm. of zinc and 15 sq. cm. of copper foil. Digest at 90° to 95°C. for 12 to 16 hr., and then boil vigorously until the volume is reduced to about 9 to 10 l.

(c) **Low-Ammonia and Alkali Water.**—Prepare 9 to 10 l. of low-ammonia water in accordance with Paragraph (b). Connect the flask with a block-tin condenser and heat on an electric heater to distill the water. Test each 100 ml. of distillate

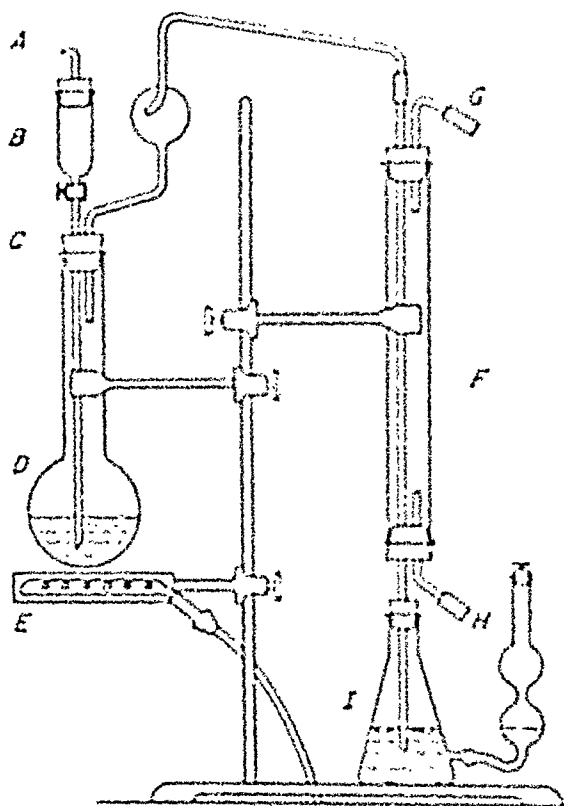


FIG. 24-10. Apparatus for Determination of Nitrogen by Distillation: A, glass hook for hanging up stopper; B, 125-ml. separatory funnel; C, special Kjeldahl rubber stopper; D, 800-ml. long-neck Kjeldahl flask; E, electric heater; F, condenser; G, water outlet; H, water inlet; I, modified Volhard nitrogen receiving flask.



(b) Transfer 0.0, 2.0, 4.0, and 6.0 ml. of the niobium solution (1 ml. = 0.1 mg. Nb to 125-ml. Phillips beakers. Treat as in the determination of niobium (preceding section), using the blank solution to adjust the instrument to zero absorbance.

(c) Calculate the slopes at 400 and 520  $m\mu$  by dividing the absorbances by the milligrams of niobium present.

(d) Determine the slopes for tungsten at 400 and 525  $m\mu$  as directed for niobium in Paragraphs (b) and (c), using 0.0, 2.0, 4.0, and 6.0 ml. of the tungsten solution (1 ml. = 0.1 mg. W).

(e) The colored compounds of the niobium and tungsten present absorb independently of each other; therefore, the following simultaneous equations may be set up.

Let:

$$A_{400} = \text{the absorbance} \times 1000 \text{ at } 400 \text{ } m\mu,$$

$$A_{520} = \text{the absorbance} \times 1000 \text{ at } 520 \text{ } m\mu,$$

$$a = \text{milligrams of niobium present,}$$

$$b = \text{milligrams of tungsten present,}$$

$$X \text{ and } X^1 = \text{slope for niobium at } 400 \text{ and } 520 \text{ } m\mu \text{ respectively, and}$$

$$Y \text{ and } Y^1 = \text{slope for tungsten at } 400 \text{ and } 520 \text{ } m\mu \text{ respectively.}$$

Then:

$$X_a + Y_b = A_{400}$$

$$X_a^1 + Y_b^1 = A_{520}$$

Solving for  $a$  and  $b$  will give formulas for calculating the milligrams of niobium and tungsten present in the sample (Note 23).

NOTE 23 *Example*—The slope for niobium is equivalent to absorbances per mg. of 1233 and 314 at wavelengths 400 and 520  $m\mu$ , respectively. The slope for tungsten is equivalent to absorbances per mg. of 331 and 361 at wavelengths 400 and 520  $m\mu$ , respectively.

Then:

$$1233a + 331b = A_{400} \text{ } m\mu$$

$$314a + 361b = A_{520} \text{ } m\mu$$

Solving for  $a$  and  $b$ :

$$a(\text{mg. Nb}) = 0.00106 A_{400} - 0.00097 A_{520}$$

$$b(\text{mg. W}) = 0.00361 A_{520} - 0.00092 A_{400}$$

(f) Calculate the per cent of niobium as follows:

$$\text{Niobium, per cent} = \frac{A}{1000} \times \frac{100}{B} \times \frac{100}{C}$$

where  $A$  = milligrams of niobium,

$B$  = weight of original sample, and

$C$  = milliliters in aliquot.

For a 2-g. sample diluted to 100 ml. and a 2-ml. aliquot taken:

$$\text{Niobium, per cent} = \frac{A}{1000} \times \frac{100}{2} \times \frac{100}{2} = A \times \frac{5}{2}$$

(g) The following order of calculations is recommended: Correct the absorbance readings for tantalum at 430 m $\mu$ , and for niobium and tungsten at 400 and 520 m $\mu$ , for the absorbances due to titanium. Calculate the per cent of niobium and tungsten (preliminary values). Based on these preliminary values, make the remaining corrections of the tantalum absorbance for the absorbances due to niobium and tungsten. Calculate the tantalum value (final). Based on the final tantalum value, correct the niobium and tungsten absorbance at 400 m $\mu$ . Calculate the niobium value (final).

## NITROGEN

### THE DISTILLATION-TITRATION METHOD

**Apparatus.**—The apparatus recommended for the determination of nitrogen by direct distillation is shown in Fig. 24-10. The apparatus consists essentially of a dropping funnel for introducing reagents, an 800-ml. long-neck Kjeldahl flask, a condenser, and a modified Volhard nitrogen receiving flask. The apparatus recommended for the determination of nitrogen by distillation with steam is shown in Fig. 24-11. The apparatus is essentially the same as that shown in Fig. 24-10, with the addition of suitable means of passing steam through the solution in the Kjeldahl flask.

**Reagents.** (a) Selenium.—Powdered selenium.

(b) Low-Ammonia Water.—Nearly fill a 12-l. flask with distilled water. Then add 4 g. of NaOH pellets and 2 g. of Devarda's alloy or 2 g. of a zinc-copper couple made by rolling together 15 sq. cm. of zinc and 15 sq. cm. of copper foil. Digest at 90° to 95°C. for 12 to 16 hr., and then boil vigorously until the volume is reduced to about 9 to 10 l.

(c) Low-Ammonia and Alkali Water.—Prepare 9 to 10 l. of low-ammonia water in accordance with Paragraph (b). Connect the flask with a block-tin condenser and heat on an electric heater to distill the water. Test each 100 ml. of distillate

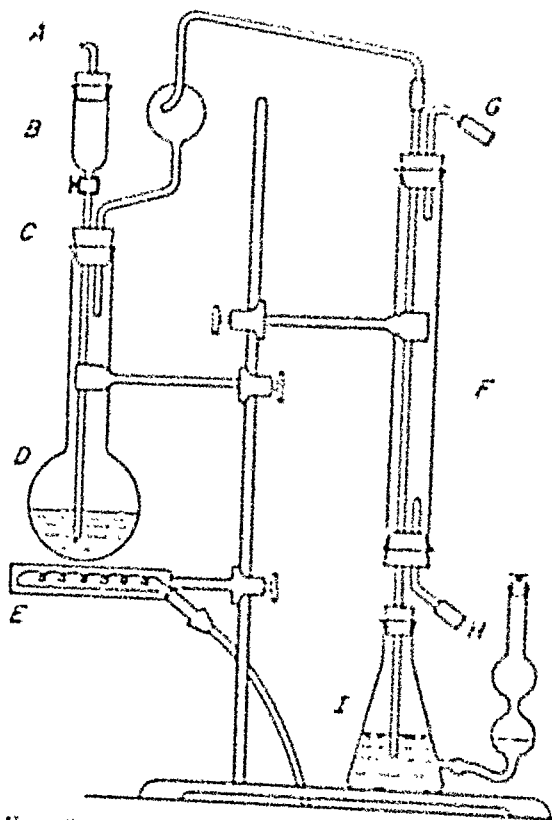


FIG. 24-10. Apparatus for Determination of Nitrogen by Distillation: A, glass hook for hanging up stopper; B, 125-ml. separatory funnel; C, special Kjeldahl rubber stopper; D, 800-ml. longneck Kjeldahl flask; E, electric heater; F, condenser; G, water outlet; H, water inlet; I, modified Volhard nitrogen receiving flask.

with Nessler reagent until the distillate is free of ammonia. Then collect the distillate in a large glass bottle.

(d) Sulfuric-Phosphoric Acid Mixture.—To 1 liter of low-ammonia water, add slowly, while stirring, 300 ml. of  $\text{H}_2\text{SO}_4$ . Cool, and add 90 ml. of  $\text{H}_3\text{PO}_4$ . The mixture shall be prepared in an atmosphere free of ammonia fumes.

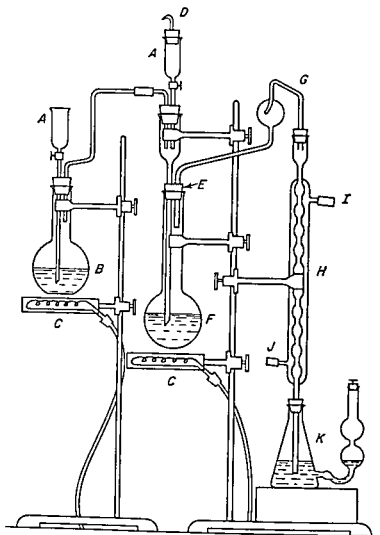


FIG. 24-11. Apparatus for Determination of Nitrogen by Distillation with Steam: *A*, 125-ml. separatory funnel; *B*, 1-liter Florence flask; *C*, electric heater; *D*, glass hook for hanging up stopper; *E*, special Kjeldahl rubber stopper; *F*, 800-ml. longneck Kjeldahl flask; *G*, nitrogen distilling head; *H*, condenser; *I*, water outlet; *J*, water inlet; *K*, modified Volhard nitrogen receiving flask.

(e) Sulfuric Acid (100%).—Mix 150 ml. of low-nitrogen, 15% fuming  $\text{H}_2\text{SO}_4$  with 200 ml. of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84).

(f) Mixed Indicator Solution.—Dissolve 0.075 g. of bromcresol green and 0.05 g. of methyl red in 100 ml. of methanol. This indicator changes from green to wine-red at pH 5.1.<sup>109</sup>

<sup>109</sup> The equivalence point of 0.1 *N* HCl and 0.1 *N*  $\text{NH}_4\text{OH}$  is at pH 5.13.

(g) **Standard Sulfuric Acid (0.01 N).**—Add 3 ml. of  $\text{H}_2\text{SO}_4$  (1:9) to 500 ml. of water and dilute to 1 liter. Standardize as follows: transfer 25 ml. of the diluted  $\text{H}_2\text{SO}_4$  to a small beaker and add 25 ml. of water and 2 drops of phenolphthalein indicator; titrate with 0.01 N NaOH to a faint persistent pink; and correct for the blank titration on the same volume.

(h) **Sodium Hydroxide Solution (333 g. per liter).**—Transfer 3 l. of distilled water to a 6-l. flask and mark the flask at the level of the liquid. Add 1000 g. of NaOH and shake the flask to dissolve the NaOH. Add 100 ml. of  $\text{BaCl}_2$  (100 g. per liter), 5 g. of Devarda's alloy or 5 g. of the zinc-copper couple (see Paragraph (b)), and 700 ml. of water. Digest at  $90^\circ$  to  $95^\circ\text{C}$ . for several hours and boil vigorously until the volume is reduced to 3 l. After the precipitate has settled, decant the nearly clear solution into a bottle provided with a glass stopper.

(i) **Standard Sodium Hydroxide Solution (0.01 N).**

**Procedure.**—(a) Transfer 5 g.<sup>110</sup> of the sample if the nitrogen content is under 0.1%, or 2 g. if the nitrogen content is 0.1% or over, to a 500- or 800-ml. Kjeldahl flask. Add 0.2 g. of powdered selenium and 50 or 70 ml. of  $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$  mixture, depending upon whether 2 or 5 g. of the sample were taken.<sup>111</sup> Heat until the sample is dissolved and then evaporate rapidly until white fumes are distinctly visible. Without cooling, rinse the neck of the flask with 10 ml. of  $\text{H}_2\text{SO}_4$  (100%). Digest 2 to 4 hr., regulating the heat so that the solution boils gently and there is a slight amount of fumes escaping at the outlet of the flask. Cool somewhat, and add 200 ml. of low-ammonia water. Stir and heat gently to dissolve salts as completely as possible. Avoid evaporation of much water. It is important that iron salts be dissolved; chromium salts will not dissolve. Continue in accordance with Paragraph (d).

(b) Some steels may not dissolve in the  $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$  mixture. If they are soluble in HCl, dissolve the sample in HCl, add  $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$  mixture, and proceed with evaporation and digestion in accordance with Paragraph (a).

(c) Some steels, notably high-cobalt, will dissolve in neither the  $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$  mixture nor HCl, but are soluble in dilute  $\text{HClO}_4$ . In this case proceed as follows: Transfer 5 g. of the sample to a 300-ml. Erlenmeyer flask. Add 30 ml. of  $\text{HClO}_4$  and 20 ml. of water. Heat on a steam bath until the sample is dissolved. Add 50 ml. of water and filter through a small paper (previously washed with low-ammonia water). Wash the paper several times with HCl (1:99) and reserve the filtrate. Place the paper in an 800-ml. Kjeldahl flask. Add 10 g. of  $\text{K}_2\text{SO}_4$ , 1 g. of  $\text{CuSO}_4$ , and 20 ml. of  $\text{H}_2\text{SO}_4$ . Heat the flask, moderately at first, and then at a temperature below the boiling point of the acid until frothing ceases. The flask should not be heated directly above the surface of the liquid. Increase the heat so as to boil the contents of the flask for 15 to 20 min. after the solution has become colorless. Cool to room temperature and add the previously reserved filtrate. Continue in accordance with Paragraph (d).

(d) Rinse the condenser, bottom stopper, and receiving flask with low-ammonia

<sup>110</sup> The weight of sample used should be regulated according to the nitrogen and chromium content. If chromium is under 0.5 g., there should be no serious bumping. If more than 0.5 g. of chromium is present, bumping may be corrected by adding a fragment or two of silica combustion tube, carborundum crystals, or similar material. If serious bumping occurs with a 5-g. sample of an 18% chromium steel, it is advisable to use a 2-g. sample.

<sup>111</sup> This method may give low results for steels containing silicon nitride, especially for the electrical steels containing more than 1.75% silicon.

and alkali water. Place 10 ml. of water, or a sufficient amount to form a seal, in the receiving flask or bulb, and add 4 drops of the mixed indicator solution. Add an amount of 0.01  $N$   $H_2SO_4$  just sufficient to turn the indicator red.<sup>112</sup> When the nitrogen content of steel exceeds 0.01%, also add to the neutralized solution 10 ml. of water, mixed indicator solution, and a measured amount of 0.01  $N$   $H_2SO_4$  approximately equivalent to the nitrogen. Tilt the receiver to ensure a seal and fit it securely to the bottom of the upright condenser by means of the rubber stopper and a suitable support. Cover the outlet of the receiver with a glass cap to prevent contamination.

(e) To an 800-ml. Kjeldahl flask add 125 ml.<sup>113</sup> of NaOH (333 g. per liter) if 50 ml. of the  $H_2SO_4$ - $H_3PO_4$  mixture were used (Paragraph (a)). Add 150 ml. of NaOH (333 g. per liter) if 70 ml. of the  $H_2SO_4$ - $H_3PO_4$  mixture were used or if the  $HClO_4$ - $H_2SO_4$  digestion (Paragraph (c)) was used. Rinse the inside and outside surfaces of the glass tubes carried by the special Kjeldahl stopper with water and then rinse, with low-ammonia water, the inside and outside surfaces of the glass parts that extend into the flask. Shake off the water and fit the stopper firmly into the neck of the Kjeldahl flask. Connect the end of the trap bulb to the upright condenser, and clamp the distilling flask firmly in place on the support.

(f) Transfer the acid solution of the steel, obtained in accordance with Paragraph (a), (b), or (c) through the separatory funnel into the distillation flask. If direct distillation (Fig. 24-10) is to be used, rinse with 75 ml. of low-ammonia water to make the total volume about 400 ml. If steam distillation (Fig. 24-11) is to be used, omit this extra portion of water. Close the top of the separatory funnel with a stopper. Adjust a proper flow of cooling water through the condenser and place the electric heater about  $\frac{1}{4}$  in. from the bottom of the Kjeldahl flask. Do not rest the flask on a ring clamp, but heat the bottom and sides of the flask. If steam distillation is used, both the Kjeldahl flask and the steam-producing flask shall be heated. Distill as rapidly as possible until 100 to 110 ml. of distillate have been collected, as indicated by a mark on the receiver. Remove the receiver and heater.

(g) If not previously done, add 4 drops of the mixed indicator to the distillate. If the solution is green, titrate with 0.01  $N$   $H_2SO_4$  to a wine-red color. Read the buret to 0.01 ml., if possible. With steels of low nitrogen content, a 5- to 10-ml. microburet is helpful.

(h) If the initial amount of 0.01  $N$   $H_2SO_4$  added to the receiving flask was in excess of the ammonia distilled (solution wine-red before titration), add from a buret sufficient 0.01  $N$  NaOH to turn the indicator green, and then add a small measured excess. Titrate with 0.01  $N$   $H_2SO_4$  as described in Paragraph (g).

(i) To obtain the equivalent of the added 0.01  $N$  NaOH, add exactly the same amount of 0.01  $N$  NaOH as before (Paragraph (h)), and again titrate with 0.01  $N$   $H_2SO_4$  to the wine-red end point.

(j) Blank.—Make a blank determination, following the same procedure and using

<sup>112</sup> W. R. Sayre, in a private communication, has shown that small amounts of ammonia are completely absorbed by water alone.

<sup>113</sup> One milliliter of the  $H_2SO_4$ - $H_3PO_4$  mixture requires for neutralization about 1.25 ml. of NaOH (333 g. per liter); 1 ml. of  $H_2SO_4$  (100%) requires about 4.5 ml. of NaOH (333 g. per liter); and 1 ml. of  $HClO_4$  requires about 1.4 ml. of NaOH (333 g. per liter). The amount of NaOH solution recommended should, therefore, provide an excess of about 15 to 20 ml.

the same amounts of all reagents. The blank should not exceed 0.3 ml. and should be uniform.

(k) Calculation.—Calculate the percentage of nitrogen as follows:

$$\text{Nitrogen, per cent} = \frac{[(A + B - C) - (D + E - F)]G \times 0.01401}{H} \times 100$$

where  $A$  = milliliters of  $\text{H}_2\text{SO}_4$  added to the absorption flask for the sample (Paragraph (d)),

$B$  = milliliters of  $\text{H}_2\text{SO}_4$  required for titration of the sample (Paragraph (g) or (h)),

$C$  = milliliters of  $\text{H}_2\text{SO}_4$  equivalent to  $\text{NaOH}$  solution added when sample is titrated in accordance with Paragraph (h) (determined in accordance with Paragraph (i)),

$D$  = milliliters of  $\text{H}_2\text{SO}_4$  added to the absorption flask for the blank,

$E$  = milliliters of  $\text{H}_2\text{SO}_4$  required for titration of the blank,

$F$  = milliliters of  $\text{H}_2\text{SO}_4$  equivalent to the  $\text{NaOH}$  solution added to the blank (determined in accordance with Paragraph (i)),

$G$  = normality of the  $\text{H}_2\text{SO}_4$ , and

$H$  = grams of sample used.

## BORON

### THE DISTILLATION-CURCUMIN (PHOTOMETRIC) METHOD (FOR PLAIN CARBON STEELS CONTAINING UNDER 0.008 PER CENT OF BORON)

*Principle of Method.*—Boron is separated by distillation as methyl borate. The isolated boric acid reacts with curcumin to form a rose-colored compound. The photometric measurement is made at approximately 510 mμ.

*Concentration Range.*—The recommended concentration range is from 0.001 to 0.008 mg. of boron in 100 ml. of solution, using a cell depth of 2 cm.<sup>114</sup>

*Stability of Color.*—The color is stable for about 1 hr.

*Interfering Elements.*—The elements ordinarily present in steel do not interfere. The analyst should exercise care to see that phosphoric acid does not spray over during the solution or distillation of the sample, as phosphoric acid will bleach the color.

*Apparatus.* (a) Apparatus for Determination of Boron by Distillation.—The apparatus shall be suitable for the distillation of methyl borate from a phosphoric acid solution of steel. A typical arrangement is shown in Fig. 24-12.

Flasks  $A$  and  $B$  shall be 100-ml., wide-neck quartz flasks.<sup>115</sup> The remainder of the apparatus, including the traps (with the exception of the condenser jackets) shall be constructed of low-boron glass.<sup>116</sup>

<sup>114</sup> This procedure has been written for a cell having a 2-cm. light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

<sup>115</sup> Three sources of supply of suitable quartz flasks are: The Amersil Co., Inc., 685 Ramsey Ave., Hillside, N. J.; The Thermal Syndicate, Inc., 12 East 46th Street, New York 17, N. Y.; and The Laboratory Equipment Corporation, Box 352, St. Joseph, Mich.

<sup>116</sup> Suitable glass for this purpose is No. 728 Corning glass or other equally low-boron glass. No. 728 Corning glass contains, according to the manufacturers' specifications, a maximum of 0.04% of  $\text{B}_2\text{O}_3$ . This should be borne in mind when making an analysis.

(b) Casseroles.—Porcelain casseroles of 300-ml. capacity, preferably new.

(c) Water Bath.—An automatically controlled water bath capable of maintaining a temperature of  $55^{\circ} \pm 3^{\circ}\text{C}$ .

(d) Filtering Crucible.—A fritted-glass crucible of fine porosity.

*Reagents.*<sup>117</sup> (a) Standard Boric Acid Solution (1 ml. = 0.002 mg. B).—Transfer 0.572 g. of  $\text{H}_3\text{BO}_3$  to a 500-ml. volumetric flask, dilute to the mark with freshly

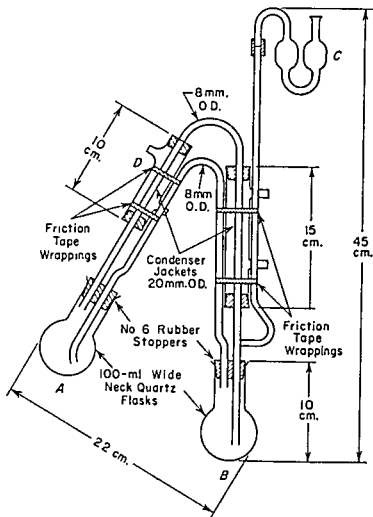


FIG. 24-12. Apparatus for Determination of Boron by Distillation: *A*, solution flask; *B*, receiving flask; *C*, trap; *D*, auxiliary condenser.

distilled water, and mix. Transfer 10 ml. of this solution to a 1-liter volumetric flask, dilute to the mark with freshly distilled water, and mix. Store in a low-boron container.

(b) Calcium Hydroxide Suspension (5.6 g. CaO per liter).—Ignite low-boron  $\text{CaCO}_3$  (0.0001% or less of boron) in a platinum dish at  $500^{\circ}$  to  $600^{\circ}\text{C}$ . Gradually raise the temperature to  $1000^{\circ}\text{C}$ . and hold at this temperature for at least 30 min. Cool, and grind in an agate mortar. Add 5.6 g. of the finely ground CaO to 1 liter of freshly distilled water, and store in a low-boron container. Thoroughly mix the solution each time before drawing off a portion for use in analysis.

<sup>117</sup> All solutions and reagents shall be stored in bottles made of low-boron glass.

(c) Low-Boron Steel.<sup>118</sup>

(d) Methanol.—Add 0.5 g. of NaOH pellets to 0.5 liter of absolute methanol, and distill in low-boron apparatus. Store in a low-boron container.

(e) Phosphoric Acid (85%).—The boron content of 10 ml. of the  $\text{H}_3\text{PO}_4$  shall not exceed 0.001 mg.<sup>119</sup>

(f) Oxalic Acid Solution.—Dissolve 50 g. of oxalic acid in 450 ml. of acetone and filter. This solution is stable for approximately two weeks.

(g) Curcumin Solution (0.25 g. per liter).—Dissolve 0.10 g. of curcumin in 400 ml. of ethanol (95%), filter,<sup>120</sup> and store, preferably in a brown low-boron bottle. This solution should be kept not longer than four weeks. One or two points on the calibration curve should be checked each time a new solution is prepared.

(h) Acetone.—Low-boron acetone.

*Preparation of Calibration Curve.*—(a) Transfer 1.0-, 2.0-, 3.0-, and 4.0-ml. aliquots of boric acid (1 ml. = 0.002 mg. B) to 100-ml. quartz flasks *A* (see Fig. 24-12). To each flask and to an additional flask to be carried through as a blank, add 5 ml. of  $\text{Ca}(\text{OH})_2$  suspension (5.6 g. CaO per liter).

(b) Evaporate the contents of the flasks to dryness. Add 0.5 g. of low-boron steel to each flask, including the blank.

(c) To a 100-ml. quartz flask *B*, add 50 ml. of methanol and 5 ml. of  $\text{Ca}(\text{OH})_2$  suspension (5.6 g. CaO per liter). To the trap *C*, add enough  $\text{Ca}(\text{OH})_2$  suspension (5.6 g. CaO per liter) to form a liquid seal. Add 10 ml. of  $\text{H}_3\text{PO}_4$  to the flask *A*, containing the sample and assemble the apparatus as illustrated in Fig. 24-12. Turn on the water supply to both the auxiliary condenser *D* and the condenser leading to flask *B*, and heat the flask containing the sample gently by means of a small burner until the reaction ceases. Remove the heat from the flask, and disconnect the water supply from the auxiliary condenser *D*.

(d) Place flask *B* in the hot water, and heat until about 25 ml. of methanol has distilled over into flask *A*. Then place both flasks in hot water, and heat so that the methanol will cycle evenly between flask *A* and flask *B* for 30 min.

(e) Remove the flasks from the water baths and transfer the solution from flask *B* and from the trap *C* to a 300-ml. porcelain casserole. Rinse the flask and trap thoroughly, first with water, then with two drops of HCl (1:9), and again with water, adding all of the washings to the casserole. Evaporate to dryness on a steam bath, remove, and cool to room temperature.

(f) To the residue in the casserole, add 1 ml. of HCl (1:4) and 5 ml. of oxalic acid solution, mix, and add 2 ml. of curcumin solution (0.25 g. per liter). When the residue in the casserole has dissolved, evaporate to dryness on a water bath at a temperature of  $55^\circ \pm 3^\circ\text{C}$ ., and bake for  $30 \pm 5$  min. at the same temperature.

(g) To the residue in the cooled casserole, add 25 ml. of acetone. After the residue has dissolved, filter through a fritted-glass crucible of fine porosity into a 100-ml. volumetric flask. Wash the crucible and contents with 25 ml. of acetone, using 3- to 5-ml. portions for each washing. Dilute the solution to 100 ml. with cold water and mix well. The color will vary from a yellowish green to a deep rose, depending upon the boron concentration.

<sup>118</sup> National Bureau of Standards standard sample No. 55 of ingot iron is satisfactory for this purpose.

<sup>119</sup> Low-boron, analytical reagent grade  $\text{H}_3\text{PO}_4$  (85%) has been found satisfactory for this purpose.

<sup>120</sup> Certain filter papers contain alcohol-soluble boron; hence, it is advisable to first wash the paper with alcohol and discard the washings.



(h) Transfer a suitable portion of the solution to an absorption cell, and measure the absorbance or transmittance at approximately 540 m $\mu$ . Compensate or correct for the blank.

(i) Plot the values obtained against milligrams of boron per 100 ml. of solution.

**Procedure.**—(a) Transfer to a 100-ml. quartz flask *A*, 0.5 g. of the sample for a steel containing 0.002% or less of boron, 0.25 g. for a steel containing 0.002 to 0.004% of boron, or 0.10 g. for a steel containing 0.001 to 0.008% of boron. Transfer to another 100-ml. quartz flask a weight of low-boron steel equal to the weight of sample taken, and carry through all steps of the procedure.

**Acid-Soluble Boron.**—(b) Proceed as directed in the preceding section (c) to (h), reserving the flask *A* (preceding section (c)) for the determination of acid-insoluble boron.

(c) Using the value obtained, read from the calibration curve the number of milligrams of boron present in the sample.

(d) **Calculation.**—Calculate the percentage of acid-soluble boron as follows:

$$\text{Acid-soluble boron, per cent} = \frac{A}{B \times 10}$$

where *A* = milligrams of boron (Paragraph (c)), and

*B* = grams of sample used.

**Acid-Insoluble Boron.**—(e) Dilute the solution in flask *A*, reserved as directed in Paragraph (b), to a volume of 90 ml. with HCl (1:8). Filter through a 9-cm., close-texture, ashless paper containing a little ashless filter paper pulp. Wash out the flask with hot HCl (2:98) and police the flask well to remove all insoluble material. Wash the residue on the filter paper, first with hot HCl (2:98) to remove the iron, and then with cold water to remove the HCl.

(f) Transfer the paper and residue to a 15- to 20-ml. platinum crucible. Add 5 ml. of Ca(OH)<sub>2</sub> suspension (5.6 g. CaO per liter), and evaporate to dryness. Ignite at 600° to 700°C. until the carbon is completely burned. Add 1 g. of Na<sub>2</sub>CO<sub>3</sub> and fuse the residue, finally tilting and heating the crucible so that the fusion is collected in a ball. Cool, remove the greater part of the fused mass by exerting a small amount of pressure on the crucible wall, and transfer the fusion to a clean, dry, quartz flask *A*. Cool to 10° to 15°C. by placing the flask in cool water. Add 4 ml. of H<sub>3</sub>PO<sub>4</sub> to the crucible, warm to dissolve the remainder of the fusion, cool, and add to flask *A*. Rinse out the crucible with two 3-ml. portions of H<sub>3</sub>PO<sub>4</sub> and add to flask *A*. Assemble the apparatus immediately as directed in the preceding section (c). Heat flask *A* to obtain complete solution of the fusion, and continue as directed in Paragraphs (b) and (c).

(g) **Calculation.**—Calculate the percentage of acid-insoluble boron as follows:

$$\text{Acid-insoluble boron, per cent} = \frac{A}{B \times 10}$$

where *A* = milligrams of boron (Paragraph (f)), and

*B* = grams of sample used.

**Total Boron.**—(h) Total boron equals the percentage of acid-soluble boron plus the percentage of acid-insoluble boron.

## BERYLLIUM

## THE OXIDE METHOD

*Reagents.* (a) Isopropyl Ether.

(b) Ammonium Chloride Wash Solution.—Dissolve 20 g. of  $\text{NH}_4\text{Cl}$  in water, add 2 or 3 drops of  $\text{NH}_4\text{OH}$  and dilute to 1 liter.

(c) Cupferron Solution (60 g. per liter).

(d) Cupferron Wash Solution.—Add 10 ml. of cupferron solution (60 g. per liter) to 1 liter of  $\text{HCl}$  (1:9).

(e) Bromcresol Purple Indicator.

(f) Hydrogen Sulfide Wash Solution.—Saturate  $\text{H}_2\text{SO}_4$  (1:99) with  $\text{H}_2\text{S}$ .

*Procedure.*—(a) Transfer at least 2 g.<sup>121</sup> of the sample, weighed to the nearest 0.01 g., to a 400-ml. beaker. Add 30 ml. of  $\text{HCl}$  and 10 ml. of  $\text{HNO}_3$ , cover, and digest until all action ceases. Finally evaporate to dryness but do not bake. Cool, add 20 ml. of  $\text{HCl}$ , and evaporate to 10 ml. Dilute to 200 ml. with hot water, heat to boiling, and boil for 5 min. Filter through an 11-cm. medium paper containing a little paper pulp into a 600-ml. beaker and wash the paper and residue about 15 times with  $\text{HCl}$  (2:98). Transfer the paper and precipitate to a platinum crucible, ignite at a low temperature to burn off the carbon of the filter paper, and reserve.

(b) Evaporate the filtrate to a sirup, add 50 ml. of  $\text{HCl}$  (5:2), and heat to boiling. Cool to  $20^\circ\text{C}$ . or below and rinse into a 300-ml. separatory funnel, using five 5-ml. portions of cold  $\text{HCl}$  (5:2). Add 150 ml. of isopropyl ether to the separatory funnel, stopper, and shake for several minutes, releasing the pressure on the stopper from time to time during the shaking. Allow the two layers to separate and draw off the acid layer into the original 600-ml. beaker. Add 25 ml. of cold  $\text{HCl}$  (5:2) saturated with isopropyl ether to the separatory funnel, stopper, and shake well. Again draw off the acid layer into the 600-ml. beaker, and discard the ether layer.

(c) Evaporate this solution to a volume of about 40 ml., add 40 ml. of  $\text{HNO}_3$  and 15 ml. of  $\text{HClO}_4$  (Caution)<sup>122</sup> in the order given, and evaporate to copious white fumes. Continue the fuming for about 5 min. to oxidize the chromium. Cool and dilute to 300 ml. with hot water. Add 5 g. of  $\text{NH}_4\text{Cl}$  and an excess of 2 to 3 ml. of  $\text{NH}_4\text{OH}$  (1:1)<sup>123</sup> and boil for 1 min. Filter through an 11-cm. medium paper containing a little paper pulp, and wash about 20 times with hot  $\text{NH}_4\text{Cl}$  wash solution. Discard the filtrate. Transfer the paper and precipitate to a 250-ml. beaker and reserve.

(d) Fuse the residue in the platinum crucible (Paragraph (a))<sup>124</sup> with 5 g. of

<sup>121</sup> This method is written to cover a range of from 0.50 to 1.30% beryllium. For steels containing from 0.05 to 0.50% beryllium, take a proportionately larger sample with increased amounts of  $\text{HCl}$  and  $\text{HNO}_3$  for solution of the sample, and of ether to remove the iron, so that the sample will contain at least 5 mg., and preferably 15 to 30 mg., of beryllium.

<sup>122</sup> Caution.—Nitric acid must always be added before adding  $\text{HClO}_4$  or serious explosions may occur.

<sup>123</sup> The excess  $\text{NH}_4\text{OH}$  specified in Paragraphs (c), (e), (g), (i), and (j) is necessary to secure complete precipitation of the beryllium.

<sup>124</sup> In the absence of tungsten and niobium, the  $\text{Na}_2\text{S}_2\text{O}_7$  fusion of the ignited residue may be leached with 200 ml. of  $\text{HCl}$  (1:19), an excess of  $\text{NH}_4\text{OH}$  added, the solution boiled and filtered, and the paper and precipitate washed with  $\text{NH}_4\text{Cl}$  wash solution. Combine this precipitate with that transferred to the 250-ml. beaker (Paragraph (c)), and complete the determination as directed in Paragraphs (f) to (h).

$\text{Na}_2\text{S}_2\text{O}_7$  at a temperature of approximately  $750^\circ\text{C}$ . Cool, and dissolve in 200 ml. of hot  $\text{HCl}$  (1:19). Add 10 ml. of  $\text{H}_2\text{SO}_3$ , boil for 10 min., and allow to settle until the supernatant liquid is clear. Filter through an 11-cm. medium paper containing a little paper pulp into a 600-ml. beaker, and wash about 15 times with  $\text{HCl}$  (2:98). Discard the precipitate.

(e) Add 2 ml. of  $\text{HNO}_3$  to the filtrate and boil for several minutes. Next add an excess of 2 to 3 ml. of  $\text{NH}_4\text{OH}$  (1:1),<sup>123</sup> boil for 1 min., filter through a 9-cm. medium paper containing a little paper pulp, and wash about 15 times with hot  $\text{NH}_4\text{Cl}$  wash solution.

(f) Transfer the paper and precipitate to the 250-ml. beaker (Paragraph (c)), add 75 ml. of  $\text{HCl}$  (1:6), stir well, and boil for about 3 min. Cool to  $20^\circ\text{C}$ . or below, add a slight excess of the cupferron solution, and stir well.<sup>123</sup> Add 1 to 2 ml. additional of cupferron solution and stir vigorously for several minutes. Filter through an 11-cm. medium paper containing a little paper pulp, using moderate suction, and wash about 15 times with cold cupferron wash solution. Discard the precipitate. Collect the filtrate and washings in a 600-ml. beaker.

(g) Evaporate to a volume of about 50 ml. Add 25 ml. of  $\text{HNO}_3$  and 5 ml. of  $\text{HClO}_4$  and evaporate to copious white fumes to destroy all organic matter. Cool, add 100 ml. of  $\text{HCl}$  (1:19), and heat to boiling. Immediately add a few drops of bromcresol purple indicator solution and  $\text{NH}_4\text{OH}$  (1:1) until the color changes to purple; then add 2 to 3 ml. in excess.<sup>123</sup> Boil for 1 min., filter through a 9-cm. medium paper containing a little paper pulp, and wash about 15 times with hot  $\text{NH}_4\text{Cl}$  wash solution.

(h) Ignite the paper and precipitate in a platinum crucible at a low temperature to burn off the paper. Cool, add 5 g. of  $\text{Na}_2\text{CO}_3$ , mix well, cover, and fuse for 15 min. at approximately  $1100^\circ\text{C}$ . Dissolve the cold melt in 100 ml. of hot water, filter through a 9-cm. medium paper containing a little paper pulp, and wash about 20 times with  $\text{NH}_4\text{Cl}$  wash solution. Ignite the paper and residue in a platinum crucible at a low temperature to burn off the carbon of the filter paper.<sup>126</sup>

(i) Fuse the residue with 5 g. of  $\text{Na}_2\text{S}_2\text{O}_7$  at a temperature of  $750^\circ$  to  $800^\circ\text{C}$ . Leach the cold melt in 100 ml. of hot  $\text{HCl}$  (1:9), add an excess of 2 to 3 ml. of  $\text{NH}_4\text{OH}$  (1:1),<sup>123</sup> and boil for 1 min. Filter through a 9-cm. medium paper containing a little paper pulp, and wash about 15 times with hot  $\text{NH}_4\text{Cl}$  wash solution. Return the paper and precipitate to the beaker, add 20 ml. of  $\text{HNO}_3$  and 10 ml. of  $\text{HClO}_4$ , and evaporate to very copious white fumes to destroy all organic matter and to dehydrate any silica present. Add 50 ml. of warm water, heat to boiling, and filter through a 9-cm. medium paper containing a little paper pulp into a 250-ml. beaker. Wash about 15 times with hot water and discard the paper.

(j) Add 2 ml. of  $\text{HCl}$  and pass in  $\text{H}_2\text{S}$  for about 20 min. to precipitate any platinum picked up from the crucible during the fusions. Filter through a 9-cm. medium paper containing a little paper pulp into a 400-ml. beaker, and wash the paper and precipitate about 15 times with  $\text{H}_2\text{S}$  wash solution. Discard the paper. Boil the filtrate for at least 10 min. to expel the  $\text{H}_2\text{S}$ , add an excess of 2 to 3 ml. of  $\text{NH}_4\text{OH}$  (1:1),<sup>123</sup> boil for 1 min., filter through a 9-cm. medium paper containing a little paper pulp, and wash about 15 times with hot  $\text{NH}_4\text{Cl}$  wash solution.

(k) Ignite the residue in platinum, first at a low temperature to burn off the

<sup>125</sup> An excess of cupferron is indicated when 1 drop forms a snow-white precipitate that rapidly disappears.

<sup>126</sup> If aluminum is present in more than trace amounts, make a second fusion with  $\text{Na}_2\text{CO}_3$  followed by leaching, filtering, etc.

paper, and finally at 1200°C. for 30 min. (to constant weight). Cool, and weigh as BeO.

(l) Calculate the percentage of beryllium as follows:

$$\text{Beryllium, per cent} = \frac{A \times 0.361}{B} \times 100$$

where  $A$  = grams of BeO, and  
 $B$  = grams of sample used.

## TIN

### THE SULFIDE-IODIMETRIC TITRATION METHOD

**Apparatus.**—When tin is to be reduced to the stannous state and determined by titration with standard iodine or iodate solution, air must be excluded during the reduction and titration to prevent oxidation of the stannous tin. This is usually accomplished by keeping the solution under a blanket of gaseous  $\text{CO}_2$ . It may be accomplished in a variety of ways. One of the simplest methods is by means of the apparatus shown in Fig. 21-13, in which the reduction of the tin solution is made in a flask capped with a rubber stopper containing an L-shape siphon tube. When reduction is complete, the end of the siphon shall be dipped into a saturated solution of  $\text{NaHCO}_3$  and set aside to cool. When cool, the stopper is removed and the solution titrated.

**Reagents.** (a) Potassium Permanganate Solution (25 g.  $\text{KMnO}_4$  per liter).

(b) Acidified Ammonium Sulfate-Hydrogen Sulfide Wash Solution.—Dissolve 50 g. of  $(\text{NH}_4)_2\text{SO}_4$  in 100 ml. of  $\text{H}_2\text{SO}_4$  (1:19). Dilute to 1 liter and saturate with  $\text{H}_2\text{S}$ .

(c) Ferric Chloride Solution (6 g.  $\text{FeCl}_3$  per liter).—Dissolve 10 g. of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in water and dilute to 1 liter.

(d) Test Lead (granular).

(e) Antimony Trichloride Solution (20 g.  $\text{SbCl}_3$  per liter).—Dissolve 2 g. of  $\text{SbCl}_3$  in 50 ml. of  $\text{HCl}$ , and dilute to 100 ml. with water.

(f) Sodium Carbonate Solution (100 g.  $\text{Na}_2\text{CO}_3$  per liter).

(g) Starch Solution (10 g. per liter).

(h) Standard Tin Solution (1 ml. = 0.001 g. Sn).

(i) Standard Potassium Iodate Solution (1 ml. = 0.0005 g. Sn).—This concentration is approximately 0.01 N. Standardize the  $\text{KIO}_3$  solution as follows: to 180 ml. of  $\text{HCl}$  (4:5) in a 300-ml. Erlenmeyer flask, add 20 ml. of  $\text{FeCl}_3$  solution, 10.0 ml. of tin solution, 10 g. of test lead, and 1 ml. of  $\text{SbCl}_3$  solution; reduce and titrate with  $\text{KIO}_3$  as directed in Paragraphs (c) and (f) of the Procedure.

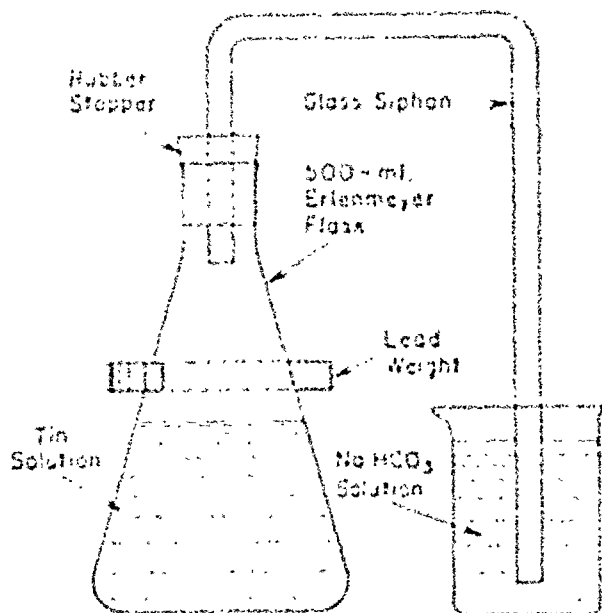


FIG. 21-13. Apparatus for Reduction of Tin.

**Procedure. 1. Steels Soluble in Nitric Acid.**—(a) Dissolve 10 g. of the sample,<sup>127</sup> weighed to the nearest 0.05 g., in a covered 750-ml. Erlenmeyer flask in 100 ml. of water and 125 ml. of  $\text{HNO}_3$  (2:3) by warming. Boil for 5 to 10 min. after solution of sample is complete. Gradually add an excess of  $\text{KMnO}_4$  solution (5 to 15 ml. usually suffices), and boil for about 5 min. Slowly add  $\text{H}_2\text{SO}_4$  until in slight excess, and then boil for 5 to 10 min. Cool to room temperature.

(b) If the steel contains tungsten or other insoluble matter, allow the solution to stand for 2 hr., add paper pulp, filter through a medium paper into a second 750 ml. Erlenmeyer flask, and wash a few times with water. Reserve the filtrate. Return the paper and precipitate to the original flask, add about 15 ml. of  $\text{H}_2\text{SO}_4$  and 20 ml. of  $\text{HNO}_3$ , heat at a moderate temperature until the paper is destroyed, and then evaporate to incipient fumes of  $\text{H}_2\text{SO}_4$ . If organic matter is indicated after the fuming treatment, add  $\text{HNO}_3$  in increments of 5 to 10 ml. followed by heating to incipient fumes until the tungstic acid is bright yellow. When the residue is completely decomposed, cool, dilute to 100 ml. with water, heat to boiling, and digest at near boiling for  $\frac{1}{2}$  to 1 hr. Add a small excess of  $\text{NH}_4\text{OH}$  and 10 to 15 g. of tartaric acid. When the tartaric acid has dissolved, again add a small excess of  $\text{NH}_4\text{OH}$  and digest at near boiling until solution is complete or nearly so (usually  $\frac{1}{2}$  to 1 hr.). Then add an excess of about 5 ml. of  $\text{H}_2\text{SO}_4$  and heat on a steam bath for  $\frac{1}{2}$  hr. Solution is generally complete at this point. If not, filter off any residue and treat again as described above, finally combining the solutions with the reserved filtrate.

(c) Dilute the solution from Paragraph (a) or (b) to about 500 ml., add paper pulp, and pass in a rapid stream of  $\text{H}_2\text{S}$  for 30 to 45 min. Let settle for 1 hr., filter on an 11-cm. medium paper, and wash with the  $(\text{NH}_4)_2\text{SO}_4\text{-H}_2\text{S}$  wash solution. Transfer the paper and precipitate to the flask, add about 15 ml. of  $\text{H}_2\text{SO}_4$  and 20 ml. of  $\text{HNO}_3$ , heat at a moderate temperature until the paper is destroyed, and then evaporate to incipient fumes of  $\text{H}_2\text{SO}_4$ . If organic matter is indicated on heating to fumes, add  $\text{HNO}_3$  in increments of 5 to 10 ml. followed by heating until the globule of sulfur is bright yellow. Two or three treatments with  $\text{HNO}_3$  generally suffices. Finally fume until all traces of  $\text{HNO}_3$  are driven off. Cool, dilute to about 100 ml. with water and boil until the solution is clear or until all soluble salts are in solution.

(d) Filter through an 11-cm. medium paper, into a 400-ml. beaker (to remove sulfur and insoluble matter) and wash with water. Dilute to 150 ml., heat to boiling, and add  $\text{KMnO}_4$  solution dropwise to the boiling solution until a permanent pink color persists. Add 20 ml. of  $\text{FeCl}_3$  solution and adjust the volume to about 200 ml. Heat to boiling, remove from the heat, add  $\text{NH}_4\text{OH}$  (1:1) to slight excess (5 to 10 ml.), and again heat to boiling. Filter on an 11-cm. medium paper and wash the beaker and paper a few times with  $\text{NH}_4\text{OH}$  (2:98), and finally 2 or 3 times with water. Dissolve the precipitate by passing 180 ml. of hot  $\text{HCl}$  (4:5) through the paper, catching the solution in a 500-ml. Erlenmeyer flask. Finally wash the paper 3 to 4 times with hot water. Repeat the precipitation of iron and tin by adding a slight excess (5 to 10 ml.) of  $\text{NH}_4\text{OH}$  (1:1). Heat to boiling and filter on an 11-cm. medium paper as previously directed. Dissolve the precipitate from the paper with 180 ml. of hot  $\text{HCl}$  (4:5) catching the solution in a 500-ml. Erlenmeyer flask. Dilute to about 350 ml., and add 10 g. of test lead and 1 ml. of  $\text{SbCl}_3$  solution.

<sup>127</sup> For steels containing up to 0.10% of tin, use 10 g. of the sample; for tin contents from 0.10 to 0.25%, use 5 g. of the sample.

(e) Stopper the flask with the rubber stopper of Fig. 21-13. Tighten the stopper in the flask, heat to boiling, and boil at a moderate rate until the solution becomes colorless; then boil 20 min. more. Remove from the heat, immerse the exit end of the glass tube in a 250-ml. beaker containing  $\text{Na}_2\text{CO}_3$  solution, and cool the solution in the flask to at least  $10^\circ\text{C}$ . Add 5 ml. of starch solution and 25 ml. of  $\text{Na}_2\text{CO}_3$  solution to the flask by means of pipets, inserting the tip between the stopper and the neck, so as to allow as little air as possible to enter the flask as it may cause low results. Titrate immediately with  $\text{KIO}_3$  solution, covering the flask with a rubber or leather washer which contains a hole through which the buret tip is inserted. Do not agitate the contents of the flask too much while titrating, but mix by gentle rotation. Titrate to the first persistent shade of blue.

(f) Correct for a reagent blank by carrying all the reagents through the same operations.

(g) Calculation.—Calculate the percentage of tin as follows:

$$\text{Tin, per cent} = \frac{(A - B)C}{D} \times 100$$

where  $A$  = milliliters of  $\text{KIO}_3$  solution required to titrate the sample,

$B$  = milliliters of  $\text{KIO}_3$  solution required to titrate the blank,

$C$  = tin equivalent of the  $\text{KIO}_3$  solution, in grams per milliliter, and

$D$  = grams of sample used.

**2. Steels Insoluble in Nitric Acid.**—(a) Transfer 10 g. of the sample to a 750-ml. Erlenmeyer flask, add 150 ml. of  $\text{HCl}$  (1:2), and dissolve by warming on a steam bath. When action ceases, carefully add  $\text{HNO}_3$  to oxidize the iron (approximately 10 ml. is required). Continue in accordance with Section (b) to (h), or (c) to (h).

## MAGNESIUM

### THE 8-HYDROXYQUINOLINE (MERCURY CATHODE) METHOD (FOR CAST IRON)

**Scope.**—This method covers the determination of magnesium in commercial cast irons that have been treated by the addition of magnesium, in the range of 0.005 to 0.25%.

**Principle of Method.**—Interfering elements are removed by an ether separation and electrolysis using a mercury cathode. After a hydrogen sulfide separation, the magnesium is precipitated as the 8-hydroxyquinolate, and finally determined gravimetrically, by weighing the precipitate, or volumetrically, by bromination with  $\text{KBrO}_3$ - $\text{KBr}$  solution.

**Reagents.** (a) Ammonium Sulfide Wash Solution.—Dilute 50 ml. of  $\text{NH}_4\text{OH}$  to 1 liter with water and saturate with  $\text{H}_2\text{S}$ .

(b) Ammonium Oxalate Solution (100 g. per liter).—Dissolve 100 g. of ammonium oxalate in 300 ml. of water and dilute to 1 liter.

(c) 8-Hydroxyquinoline Solution (40 g. per liter).—Dissolve 40 g. of 8-hydroxyquinoline in 200 ml. of acetic acid (1:4), and dilute to 1 liter with acetic acid (1:4). Filter before use, and prepare fresh as needed.

(d) Potassium Bromate-Bromide Solution (0.05 N).—Dissolve 1.3917 g. of  $\text{KBrO}_3$  and 5 g. of  $\text{KBr}$  in water, and dilute to 1 liter in a volumetric flask (1 ml. = 0.000152 g. Mg). This is a primary standard.

(e) **Sodium Thiosulfate Solution (0.05 N).**—To standardize, pipet 25 ml. of 0.05 N  $\text{KBrO}_3$ -KBr solution into a 125-ml. flask. Add 30 ml. of water, 2 g. of KI, and 10 ml. of HCl (1:1). Titrate with  $\text{Na}_2\text{S}_2\text{O}_3$  solution to a light straw color, add 2 ml. of starch solution, and continue titration to disappearance of the blue color.

(f) **Starch Solution.**

(g) **Iron (Magnesium-Free).**—Less than 0.001% magnesium.

**Procedure.**—(a) Transfer 5 g. of the sample to a 400-ml. beaker. Add 10 ml. of HCl (1:1) and heat until action ceases. Carefully add 15 ml. of  $\text{HNO}_3$  (1:1) to oxidize the iron, and evaporate to dryness. Cool, add 25 ml. of HCl, and again evaporate to dryness. Add 25 ml. of HCl, cover, and digest until salts are in solution.

(b) Transfer the solution to a separatory funnel, rinsing the beaker with HCl (1:1). Add 200 ml. of ethyl ether to the funnel, stopper, and shake vigorously. Allow the layers to separate, draw off the acid layer, and gently evaporate (avoid free flames) to 5 ml. to remove the ether. Add 20 ml. of  $\text{HNO}_3$  and 10 ml. of  $\text{HClO}_4$ , and evaporate to copious white fumes (Caution). Cool, add 50 ml. of hot water, and stir to dissolve the salts. Filter through a coarse-texture paper and wash the paper and residue 10 times with hot water. Discard the residue.

(c) Transfer the filtrate to a mercury cathode cell, and electrolyze at 3 to 20 amp. per sq. dm., depending upon the type of cell, until the bulk of the iron has been removed. Transfer the solution from the cell to a 250-ml. beaker with the current still flowing, rinsing the cell three times with 10-ml. portions of water. To the solution add 0.3 g. of  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , and then  $\text{NH}_4\text{OH}$  (1:1) until neutral to litmus paper; finally, add 10 ml. in excess. Pass a rapid stream of  $\text{H}_2\text{S}$  through the solution for 20 min. and allow the precipitate to settle. Filter through a fine-texture paper into a 400-ml. beaker and wash 10 times with  $\text{NH}_4\text{OH}$ - $\text{H}_2\text{S}$  wash solution. Discard the precipitate.

(d) Add HCl (1:1) to the filtrate until neutral to litmus, and then add an excess of 20 ml. Boil the filtrate down to a volume of 25 ml. to remove  $\text{H}_2\text{S}$ . Add 10 ml. of ammonium oxalate solution and  $\text{NH}_4\text{OH}$  (1:1) until the solution is neutral to litmus. Add an excess of 10 ml., allow to stand for 1 to 2 hr. at room temperature (approximately  $70^\circ\text{C}.$ ), and filter through a coarse-texture paper, to remove any precipitate which may have formed, into a 400-ml. beaker. Wash the paper and precipitate 6 times with cold ammonium oxalate wash solution and discard the precipitate.

(e) Make the filtrate just acid to litmus with HCl (1:1), heat to  $60^\circ$  to  $70^\circ\text{C}.$ , and add 10 ml. of 8-hydroxyquinoline solution. Add  $\text{NH}_4\text{OH}$  (1:1) until neutral to litmus and an additional 10 ml. in excess. Stir vigorously and let stand for 30 min. to allow the precipitate to settle. Filter on a weighed fritted-glass or porcelain crucible and wash 10 times with hot  $\text{NH}_4\text{OH}$  (2:98). Then proceed by either Paragraph (f) or (h).

(f) Dry the precipitate at  $160^\circ\text{C}.$  to constant weight and weigh as magnesium 8-hydroxyquinolate.

(g) **Calculation:**

$$\text{Magnesium, per cent} = \frac{(A - B) \times 0.0778}{C} \times 100$$

where  $A$  = grams of magnesium 8-hydroxyquinolate,

$B$  = weight of blank, in grams, and

$C$  = grams of sample used.

(h) Dissolve the washed precipitate in 30 ml. of hot HCl (1:1) into a 250-ml. beaker, by pouring successive portions through the crucible, and then wash the crucible thoroughly with hot water. Cool the solution to room temperature, dilute to 150 ml., and add from a buret an exactly measured volume of 0.05 *N* KBrO<sub>3</sub>-KBr solution sufficient to provide an excess of 5 ml. Add 2 g. of KI and titrate immediately with 0.05 *N* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution to a light straw color, then add 2 ml. of starch solution and continue the titration to the disappearance of the blue color. Make the titration rapidly enough so that the elapsed time from addition of the KBrO<sub>3</sub>-KBr solution to the end point of the titration does not exceed 2 min.

(i) Blank.—Make the blank determination using magnesium-free iron, following through all the steps of the procedure and using the same amounts of all reagents, including exactly the same volume of KBrO<sub>3</sub>-KBr solution as was needed for the unknown.

(j) Calculation.—Calculate the percentage of magnesium as follows:

$$\text{Magnesium, per cent} = \frac{(A - B)C \times 0.00304}{D} \times 100$$

where *A* = milliliters of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution required to titrate the blank,

*B* = milliliters of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution required to titrate the sample,

*C* = normality of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution, and

*D* = grams of sample used.



until the solution turns brown and slightly cloudy. Stir thoroughly and then add  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  to dissolve the brown color (1 g. should be enough). Allow the white cerium oxalate to settle overnight, then filter on a double paper of medium porosity and wash thoroughly with an  $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{-H}_2\text{C}_2\text{O}_4\text{-H}_2\text{O}$  solution (2.5 g.:1 g.:500 ml.). Ignite the precipitate carefully to rare earth oxides in a tared crucible. Cool and weigh.

An alternate procedure is to dissolve a sample in 6 *N*  $\text{H}_2\text{SO}_4$ , filter into a polyethylene beaker, dilute to 100 ml., add 46% HF and paper pulp, heat 10 to 20 min. to precipitate the rare earth fluorides, filter, wash the precipitate with  $\text{H}_2\text{SO}_4\text{-HF}$  (1:100), ignite as above.

### CERIUM AND LANTHANUM (PHOTOMETRIC) METHOD<sup>131</sup>

*Apparatus.* Spectrophotometer with Flame Photometer Attachment.  
Mercury Cathode Cell.

*Procedure.*—Dissolve a 3 g. sample in 40 ml. of HCl (1:1) with heating. Oxidize the solution carefully with 5 ml. of  $\text{HNO}_3$ , then add 30 ml.  $\text{HClO}_4$ , and evaporate until white fumes occur. Cool, add 100 ml. of  $\text{H}_2\text{O}$  to dissolve iron salts, filter and wash the paper and residue with HCl (1:20). Retain the filtrate (NOTE 24).

NOTE 24.—Tungsten must be removed, if present, to prevent loss of rare earths by adsorption.

Transfer the paper and contents to a platinum crucible and ash. Heat the ashed residue with 2 ml. of HF and 2 ml.  $\text{HClO}_4$  until white fumes appear. Cool, dilute with water, and add to the acid solution that will be left from the methyl isobutyl ketone extraction. Transfer the original solution to a separatory funnel containing 20 to 30 ml. of HCl (8 *N*). Add 50 to 60 ml. of methyl isobutyl ketone and extract the iron and chromium into the organic layer. Repeat extractions until the organic layer is almost colorless. Two to three extractions should be sufficient.

Transfer the aqueous solution to a beaker, add 10 ml. each of  $\text{HNO}_3$  and  $\text{HClO}_4$  and evaporate to white fumes. Cool, dilute to 50 ml., transfer to a mercury cathode cell, and electrolyze until the iron, chromium, and nickel are completely removed from the solution. Filter the electrolyte into a 500-ml. polyethylene beaker, wash with  $\text{HClO}_4$  (1:100); add 10 ml. of  $\text{HClO}_4$  and 20 ml. of HF, dilute to 100 to 150 ml. and heat at 70° to 80°C. for 30 min. on the water bath to precipitate the rare earths. Filter, wash the precipitate with HF (1:100) and  $\text{H}_2\text{O}$ , transfer the precipitate to a weighed platinum crucible and ignite. The weight of the residue is the total rare earth elements as oxides. Dissolve the oxides in 2 ml. of  $\text{H}_2\text{SO}_4$  (1:1), transfer to a 50-ml. flask and dilute to the mark. Determine cerium and lanthanum according to the following procedures.

*Cerium.*—To a measured volume of the acid solution (5 to 10 ml.), add 6 ml. of  $\text{H}_2\text{SO}_4$  (1:1), and 1 ml. of  $\text{AgNO}_3$  (0.16 g. per liter); dilute to 80 ml. Add 200 mg. of  $\text{K}_2\text{S}_2\text{O}_8$ , heat gently, then boil to destroy the excess  $\text{K}_2\text{S}_2\text{O}_8$ . Cool, transfer to a 100-ml. volumetric flask, and dilute to the mark. Transfer 10 ml. of this solution, 20 ml. of  $\text{H}_2\text{O}$ , 2 ml. of methylene blue (0.01% in  $\text{H}_2\text{O}$ ), 10 ml. of benzene, and 10 ml. of KOH (2 *N*) to an extraction funnel and shake. Transfer the benzene layer, which now contains the cerium, to a spectrophotometer cell and measure its absorbance at 510  $\text{m}\mu$ , compared to pure benzene. From a calibration

<sup>131</sup>Takeyama, Shuro, Sudo, Emiko, and Goto, Hidehiro, Sci. Rep. RITU, A, 12, 401-22, 1960.

# OTHER METHODS

## THE DETERMINATION OF RARE EARTHS

*Summary of Method.*—For low chromium and carbon steels, cerium is oxidized without prior separation of iron, and titrated with ferrous sulfate. After separation of the rare earth elements from iron and alloying elements, the rare earths are precipitated as the oxalate or fluoride, ignited to the oxide and weighed, or determined photometrically.<sup>128</sup>

### CERIUM BY OXIDATION REDUCTION TITRATION

*Procedure.*—Dissolve a sample (5 to 10 g.) with 100 ml. of mixed acid (150 ml.  $\text{H}_2\text{SO}_4$  - 150 ml.  $\text{H}_3\text{PO}_4$  - 700 ml.  $\text{H}_2\text{O}$ ) with gentle heating. Remove the beaker from the heat and oxidize the solution carefully with  $\text{HNO}_3$  (8 to 10 ml. will be required), boil for 2 or 3 min., and filter through a pad of pulped filter paper into a 500 ml. wide-mouthed Erlenmeyer flask. Wash with hot  $\text{H}_2\text{SO}_4$  (1:100), dilute to 350 to 400 ml. with hot water, add a few boiling chips and, while boiling, add  $\text{KMnO}_4$  (2%) dropwise, until a slight excess persists. Boil for 5 to 10 min., destroy the excess  $\text{KMnO}_4$  by adding  $\text{HCl}$  (1:1) and boil 5 to 10 min. longer. Cool to room temperature. Dilute to 500 ml., mix thoroughly and divide into two equal portions. To portion *A*, add 5 ml. of  $\text{NaNO}_2$  (1%) and 2 g. of urea; allow to stand for 5 min. To both portions *A* and *B* add a few drops of diphenylamine sulfonate indicator and titrate with standard  $\text{Fe}(\text{NH}_4)\text{SO}_4$  (0.03 N) until the purple color changes to green; add an excess of 5 ml. and back titrate with standard  $\text{K}_2\text{Cr}_2\text{O}_7$  (0.03 N).

The solution consumed in reduction of *A* is equivalent to the chromium and vanadium in the sample; that consumed by *B* is equivalent to these two elements plus cerium. The difference is due to the cerium content.

### COMBINED RARE EARTHS (GRAVIMETRIC) METHOD<sup>129,130</sup>

*Procedure.*—Weigh a 2 to 3 g. sample into a 600-ml. beaker. Dissolve in 100 ml.  $\text{H}_2\text{SO}_4$  (1:5), evaporate to 70 ml., and cool. Add 10 to 12 g. of  $\text{Na}_2\text{O}_2$  slowly and carefully with stirring. Dilute with  $\text{H}_2\text{O}$  to 100 ml. and evaporate down to 70 ml. again. Add 40 ml. of  $\text{H}_2\text{O}$ , stir in a small amount of filter paper pulp, and filter the precipitate through double, tight filter papers. Do not wash the precipitate. Dissolve the precipitate with 30 ml. of hot  $\text{H}_2\text{SO}_4$  (1:7), added in small portions. Wash the filter thoroughly with  $\text{H}_2\text{O}$  containing a few drops of  $\text{H}_2\text{SO}_4$  (1:7) into a 600 ml. beaker. Dilute to 300 ml., add 50 ml. of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  (50 g. of the oxalate dissolved in 1 liter of  $\text{H}_2\text{O}$  and filtered before using) and then  $\text{NH}_4\text{OH}$ .

<sup>128</sup> Fritz, James S., Richard, Marlene Johnson, and Lane, William J., *Anal. Chem.*, **30**, 1776-9, 1958.

<sup>129</sup> Johnson, C. Morris, *The Iron Age*, 94-6, January 17, 1952.

<sup>130</sup> Watanabe, Shiro, *Japan Analyst*, **9**, 736-41, 1960.

until the solution turns brown and slightly cloudy. Stir thoroughly and then add  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  to dissolve the brown color (1 g. should be enough). Allow the white cerium oxalate to settle overnight, then filter on a double paper of medium porosity and wash thoroughly with an  $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{-H}_2\text{C}_2\text{O}_4\text{-H}_2\text{O}$  solution (2.5 g.:1 g.:500 ml.). Ignite the precipitate carefully to rare earth oxides in a tared crucible. Cool and weigh.

An alternate procedure is to dissolve a sample in 6 *N*  $\text{H}_2\text{SO}_4$ , filter into a polyethylene beaker, dilute to 100 ml., add 46% HF and paper pulp, heat 10 to 20 min. to precipitate the rare earth fluorides, filter, wash the precipitate with  $\text{H}_2\text{SO}_4\text{-HF}$  (1:100), ignite as above.

### CERIUM AND LANTHANUM (PHOTOMETRIC) METHOD<sup>131</sup>

*Apparatus.* Spectrophotometer with Flame Photometer Attachment.  
Mercury Cathode Cell.

*Procedure.*—Dissolve a 3 g. sample in 40 ml. of HCl (1:1) with heating. Oxidize the solution carefully with 5 ml. of  $\text{HNO}_3$ , then add 30 ml.  $\text{HClO}_4$  and evaporate until white fumes occur. Cool, add 100 ml. of  $\text{H}_2\text{O}$  to dissolve iron salts, filter and wash the paper and residue with HCl (1:20). Retain the filtrate (NOTE 24).

NOTE 24.—Tungsten must be removed, if present, to prevent loss of rare earths by adsorption.

Transfer the paper and contents to a platinum crucible and ash. Heat the ashed residue with 2 ml. of HF and 2 ml.  $\text{HClO}_4$  until white fumes appear. Cool, dilute with water, and add to the acid solution that will be left from the methyl isobutyl ketone extraction. Transfer the original solution to a separatory funnel containing 20 to 30 ml. of HCl (8 *N*). Add 50 to 60 ml. of methyl isobutyl ketone and extract the iron and chromium into the organic layer. Repeat extractions until the organic layer is almost colorless. Two to three extractions should be sufficient.

Transfer the aqueous solution to a beaker, add 10 ml. each of  $\text{HNO}_3$  and  $\text{HClO}_4$  and evaporate to white fumes. Cool, dilute to 50 ml., transfer to a mercury cathode cell, and electrolyze until the iron, chromium, and nickel are completely removed from the solution. Filter the electrolyte into a 500-ml. polyethylene beaker, wash with  $\text{HClO}_4$  (1:100); add 10 ml. of  $\text{HClO}_4$  and 20 ml. of HF, dilute to 100 to 150 ml. and heat at 70° to 80°C. for 30 min. on the water bath to precipitate the rare earths. Filter, wash the precipitate with HF (1:100) and  $\text{H}_2\text{O}$ , transfer the precipitate to a weighed platinum crucible and ignite. The weight of the residue is the total rare earth elements as oxides. Dissolve the oxides in 2 ml. of  $\text{H}_2\text{SO}_4$  (1:1), transfer to a 50-ml. flask and dilute to the mark. Determine cerium and lanthanum according to the following procedures.

*Cerium.*—To a measured volume of the acid solution (5 to 10 ml.), add 6 ml. of  $\text{H}_2\text{SO}_4$  (1:1), and 1 ml. of  $\text{AgNO}_3$  (0.16 g. per liter); dilute to 80 ml. Add 200 mg. of  $\text{K}_2\text{S}_2\text{O}_8$ , heat gently, then boil to destroy the excess  $\text{K}_2\text{S}_2\text{O}_8$ . Cool, transfer to a 100-ml. volumetric flask, and dilute to the mark. Transfer 10 ml. of this solution, 20 ml. of  $\text{H}_2\text{O}$ , 2 ml. of methylene blue (0.01% in  $\text{H}_2\text{O}$ ), 10 ml. of benzene, and 10 ml. of KOH (2 *N*) to an extraction funnel and shake. Transfer the benzene layer, which now contains the cerium, to a spectrophotometer cell and measure its absorbance at 510  $m\mu$ , compared to pure benzene. From a calibration

<sup>131</sup> Takeyama, Shuro, Sudo, Emiko, and Goto, Hidehito, Sci. Rep. RITU, A, 12, 401-22, 1960.

curve prepared in the same manner, using known amounts of cerium, the cerium content of the sample is read.

**Lanthanum.**—Introduce a portion of the total oxide solution into the flame photometer and measure the intensity at 442 m $\mu$ . A slit width of 0.10 mm., an oxygen pressure of 15.0 and a hydrogen pressure of 2.0 lbs. per sq. in. can be used. Measure the background at 450 m $\mu$  and subtract it from the measured value at 442 m $\mu$ . Obtain the amount of lanthanum from a calibration curve prepared in the same way with known amounts of lanthanum.

## THE DETERMINATION OF ARSENIC

**Summary of the Method.**—In most methods, arsenic is separated from iron, following solution of the sample, by distillation as arsenic trichloride. Arsenic in the distillate is then determined by a volumetric procedure, by weighing as As<sub>2</sub>S<sub>3</sub>, or photometrically.

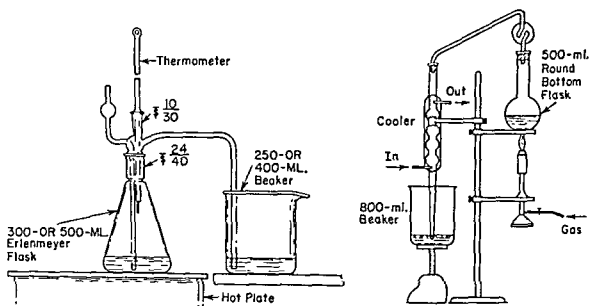


FIG. 24-14. Apparatus for Determination of Arsenic by Distillation.

Alternatively, elemental arsenic is precipitated by hypophosphite, dissolved and determined iodometrically.

**Procedure. Distillation Method.**—Dissolve a sample (generally, about 10 g. should be used) in 150 ml. of HNO<sub>3</sub> (1:3); control the temperature so that the reaction does not become too violent. Cool, add 50 ml. of H<sub>2</sub>SO<sub>4</sub>, and evaporate to fumes, cool, wash down the sides of the beaker and again heat until fumes of H<sub>2</sub>SO<sub>4</sub> appear. Cool, carefully add 50 ml. of H<sub>2</sub>O to the residue, and again cool to room temperature. Transfer to a distilling flask (Fig. 24-14) by means of 150 to 175 ml. of HCl; add about 20 g. of CuCl<sub>2</sub> (or FeSO<sub>4</sub>·7H<sub>2</sub>O). Distill until 100 ml. of distillate have been collected in 100 ml. of water contained in a 400-ml. beaker immersed in an ice bath. The temperature of the vapor in the distillation flask must be kept below 107°C. if there is antimony in the steel. After completion of the distillation, pass a rapid stream of H<sub>2</sub>S through the distillate to precipitate the As<sub>2</sub>S<sub>3</sub>. Allow to stand at least 1 hr., filter on a weighed Gooch crucible,

evaporate at 90°C. to 50 ml.; add 50 ml. of  $\text{H}_2\text{O}$ , 15 ml.  $\text{SO}_2$  saturated  $\text{H}_2\text{O}$ , 10 ml. hydrazine hydrochloride (15%), and then 25 ml. more of  $\text{SO}_2$  saturated water. Boil for 5 min., allow the precipitate to settle, filter through a tared, sintered glass filter, wash with hot water, and then with alcohol. Dry at 105°C., and weigh as elemental tellurium.

## THE DETERMINATION OF URANIUM

*Summary of the Methods.*—Uranium may be isolated from the steel matrix in a sulfuric acid solution by adsorption on a strong base ion exchange resin, interfering cations washed with hydrochloric acid, and the uranium eluted from the resin with 2.0 *M* perchloric acid. Residual iron can be removed from the eluted solution by extraction with cupferron or deposition in a mercury cathode. The resulting solution may be analyzed fluorophotometrically or polarographically. This method is best suited to determination of residual amounts (a few micrograms) of uranium.

For larger concentrations, the uranium may be separated from the iron in sulfuric acid solution by precipitation with ammonium hydroxide, the remaining iron, titanium, vanadium, and zirconium precipitated with cupferron in a strong sulfuric acid solution in which the uranium is hexavalent. The uranium may then be reduced to the quadrivalent form and precipitated as the cupferrate, the precipitate dried, ignited, and weighed as  $\text{U}_3\text{O}_8$ .

## THE ION EXCHANGE (FLUOROPHOTOMETRIC) METHOD<sup>132, 133</sup>

*Reagents.* a. Resin (IRA-400).—Prepare by extracting 200 g. for 24 hr. with 1 liter of methyl alcohol. Then extract successively with 2 l. each of  $\text{H}_2\text{O}$ , NaOH (1 *N*), NaOH (3 *N*), HCl (1 *N*), HCl (3 *N*), and finally  $\text{H}_2\text{O}$ . Transfer a quantity of the wet resin to an ion exchange column. Convert to the chloride form by passing through 4 l. of HCl (1.0 *N*). Convert the resin to the sulfate form by passing through  $\text{H}_2\text{SO}_4$  (10%), until the effluent is 10%  $\text{H}_2\text{SO}_4$ . Check by titrating an aliquot of effluent with standard NaOH. Wash the column with  $\text{H}_2\text{O}$  until effluent is free from sulfate.

*Regeneration of Resin.*—Backwash the column with  $\text{H}_2\text{O}$ . Elute with 2 l. of HCl (1 *N*). Reconvert to sulfate form in the same way as in preparation of the resin.

*Procedure.*—Dissolve a 10 g. sample in a platinum dish by adding successively 1 to 2 ml.  $\text{H}_2\text{O}$ , 10 ml. HF and  $\text{HNO}_3$  (1:3), gradually until the reaction stops. Heat gently to complete the solution of the sample. Add 12 ml. of  $\text{H}_2\text{SO}_4$ , and enough  $\text{H}_2\text{O}$  to make a volume of about 200 ml. Evaporate to dryness. Cool, add 150 ml. of  $\text{H}_2\text{O}$  and 12 ml.  $\text{H}_2\text{SO}_4$ . Heat to dissolve the residue and evaporate to about 150 ml. Filter. Dilute filtrate and washings to 200 ml., and divide into two 100 ml. portions. Add 15 ml. of  $\text{H}_2\text{SO}_4$  to each aliquot, and dilute to 200 ml. Add this solution to the resin column from a separatory funnel at a rate of about 2 ml. per min. Pass through HCl (0.05 *M*) at a rate of 5 ml. per min. until the effluent will give no reaction for iron by the KCNS test. Elute the

<sup>132</sup> Price, George R., Ferretti, Renato J., and Schwartz, Samuel, *Anal. Chem.*, **25**, 322–31, 1953.

<sup>133</sup> Welford, George A., and Sutton, Doris, N.Y.O.-4755, 1957, U. S. Atomic Energy Commission Report.

Alternatively, high tungsten steels may be dissolved in HCl (1:1), the tungsten precipitated as the yellow oxide by addition of  $\text{HNO}_3$ , most of the iron removed by an ether extraction, and the uranium determined by the cupferron precipitations as described before.

### THE DETERMINATION OF ZINC

*Summary of the Method.*—Zinc, generally present in amounts of less than 0.1% in steels, of less than 0.5% in ores, or in the iron-zinc alloy on galvanized steel, may be determined, after separation from most of the iron, by precipitation as the sulfide or phosphate, ignited to the oxide and weighed. Use of rubber, which may contain zinc, should be avoided. Care is necessary in igniting the zinc sulfide or phosphate to avoid volatilizing zinc.

*Procedure.*—Dissolve a 10 g. sample in 100 ml. of  $\text{H}_2\text{SO}_4$  (1:9) with warming. Filter, dilute the filtrate to 250 ml., cool, and add  $\text{Na}_2\text{CO}_3$  (saturated) to the formation of a precipitate that persists; clear with a minimum of  $\text{H}_2\text{SO}_4$  (1:9). Pass in  $\text{H}_2\text{S}$  for 20 to 30 min., allow the precipitate to settle, filter, and wash with dilute (1:100)  $\text{H}_2\text{SO}_4$ , saturated with  $\text{H}_2\text{S}$ . Discard the filtrate. Ignite the precipitate slowly at a temperature below  $500^\circ\text{C}$ . Dissolve the ignited residue in a minimum of HCl (1:1), add 5 ml. of  $\text{H}_2\text{SO}_4$  (1:1), evaporate to fumes, dilute to 40 ml.; again pass in  $\text{H}_2\text{S}$  for 15 to 20 min., allow to settle, filter, and wash as before. Discard the precipitate.

Neutralize the filtrate with  $\text{NH}_4\text{OH}$  (to methyl red end point), add 10 ml. of 0.1 N  $\text{H}_2\text{SO}_4$ , dilute to 100 ml., and pass in  $\text{H}_2\text{S}$  for 20 to 30 min., filter, and wash. Discard the filtrate. Dissolve the precipitated sulfides in HCl (1:1), evaporate to 40 to 50 ml., add 5 g.  $\text{NH}_4\text{Cl}$ , 10 ml. of sodium acetate (2 N), and dilute to 150 ml. Heat on the water bath, add 10 ml. of  $(\text{NH}_4)_2\text{HPO}_4$  (10%) slowly with stirring. Cover the beaker and continue to heat for 2 hrs. Filter through a Gooch or sintered glass crucible, wash with about 150 ml. of cold water, and 5 ml. of  $\text{C}_2\text{H}_5\text{OH}$ , dry at  $105^\circ\text{C}$ . to constant weight, and weigh. The weight of the dried precipitate,  $\text{ZnNH}_4\text{PO}_4$ , can be converted to zinc; the precipitate can be ignited carefully at  $900^\circ\text{C}$ . to  $\text{Zn}_3\text{P}_2\text{O}_7$ . The zinc content, as calculated from the weight of each of these compounds, should agree.

## Chapter 25

# ALLOYS: FERRO-ALLOYS

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**Introduction.**—This chapter comprises methods compiled under the jurisdiction of Committee E-3 on Chemical Analysis of Metals, American Society for Testing and Materials, Philadelphia 3, Pa. Standard and Tentative Methods for Sampling and Analysis are included. Both Standard and Tentative Methods are issued under a fixed designation E-30, followed by a number that is the year of original adoption or, in the case of revision, the year of last revision; the year is followed by a T for Tentative Methods. The designation E30-60T, for example, denotes a Tentative Method, adopted in 1960.

More extensive information, such as may be necessary for unusual or research analytical problems, is available in several published works.<sup>1</sup>

<sup>1</sup>ASTM, Methods for Chemical Analysis of Metals, American Society for Testing and Materials, Philadelphia, 1960; Beeghly, H. F., Ferrous Metallurgy, Reviews, Analytical Chemistry, 21, 241-6, 1949; 22, 235-8, 1950; 23, 228-31, 1951; 24, 252-8, 1952; 25, 30-6, 1953; 27, 611-14, 1955; 29, 638-43, 1957; 31, 706-12, 1959; 33, 70R-76R, 1961; BSI, Methods for the Sampling and Analysis of Iron and Steel, British Standards Institution, London (as issued); Kolthoff, I. M., and Elving, P. J. (eds.), Treatise on Analytical Chemistry, Interscience Publishers, New York, 1961; Lundell, G. E. F., Hollman, J. L., and Bright, H. A., Chemical Analysis of Iron and Steel, John Wiley and Sons, Inc., New York, 1931; Piggott, E. C., Ferrous Analysis—Modern Practice and Theory, John Wiley and Sons, New York, 1953; Iron and Steel Institute, Special Report #68, The Determination of Gases in Metals, The Iron and Steel Institute, London, 1960; Westwood, W., and Mayer, A., Chemical Analysis of Cast Iron, and Foundry Materials, Allen and Unwin, 1952.

# STANDARD METHODS FOR CHEMICAL ANALYSIS OF FERRO-ALLOYS<sup>2</sup>

## SAMPLING (E32-42)

*Scope.*—(a) These methods include procedures for the sampling of the various ferro-alloys, either before or after shipment from the plants of the manufacturers. They are designed to give results representative of each lot that will be comparable with the manufacturer's guaranteed analysis for the same lot. For check analysis, the purchaser may use any sampling procedure he desires, but the analytical results obtained on such samples shall not be a basis for complaint or rejection, unless the procedure followed is of an accuracy equivalent to that prescribed in these methods.

(b) In sampling ferro-alloys, serious errors often occur from contamination of the samples by iron from the sampling appliances. Therefore, special precautions should be observed to avoid this source of error. Metallic iron may be removed with a magnet from nonmagnetic alloys; its estimation in other alloys requires special analytical procedures (NOTE 1). To avoid this error, parts of crushers and pulverizing equipment contacting the samples shall be of steel or other material showing a high resistance to abrasion of the type involved.

NOTE 1.—Metallic iron in ferrochromium and ferrosilicon may be determined as follows: transfer 5 g. of the sample of alloy to a 150-ml. beaker; add 25 ml. of  $\text{HNO}_3$  (1:3); cover; boil 5 min; filter into a 250 ml. beaker; and wash with hot water; add  $\text{NH}_4\text{OH}$  in slight excess; heat to boiling, filter; and wash with hot water; dissolve the precipitate on the paper with a minimum quantity of hot  $\text{HCl}$  (1:2); wash the filter with hot water; and titrate the iron by a standard procedure. Multiply the iron value of the total number of milliliters of titrating solution used by 100 and divide by 5 to find the percentage of metallic iron.

*Apparatus for Preparing Samples.*—The following equipment is required for the preparation of analytical samples of ferro-alloys:

(a) *Crusher.*—A strongly built jaw crusher capable of rapidly crushing 1-in. lumps to sizes  $\frac{1}{4}$ -in. and smaller shall be used. The crushing plates of this machine shall be made of a hard and abrasion-resistant steel, such as manganese steel or a properly hardened alloy or hypereutectoid carbon steel.

(b) *Roll Crusher.*—A roll crusher, the rolls of which are fitted with tires of hardened and tempered chromium steel to avoid iron contamination of the sample, shall be used to reduce the  $\frac{1}{4}$ -in. pieces to a particle size that will pass the No. 10 (2000- $\mu$ ) sieve and be retained on the No. 20 (840- $\mu$ ) sieve.

(c) *Riffles.*—Riffles, also designated as Jones dividers, are usually preferable to the use of hand methods for dividing samples. Riffles with openings of  $\frac{1}{2}$  in., 1 in., 2 in., and 3 in. should be available; the  $\frac{1}{2}$ -in. riffle to be used for samples containing particles up to  $\frac{1}{8}$  in. in size, the 1-in. riffle for samples containing particles

<sup>2</sup> ASTM Designation: E31-58. Reproduced with the permission of the American Society for Testing and Materials.



up to  $\frac{3}{8}$  in., the 2-in. for samples containing particles up to  $\frac{3}{4}$  in., and the 3-in. for samples containing particles up to 2 in. in size. Riffles should be of the enclosed type to reduce dust losses. The use of multiple riffles is not approved.

(d) Mortar and Pestle.—The mortar and pestle shall both be made of properly hardened alloy steel of a kind and grade designed to resist severe abrasive forces (NOTE 2). Suitable dimensions of the mortar are  $3\frac{1}{8}$  in. in outside height, 3 in. in outside diameter,  $1\frac{1}{16}$  in. in inside diameter, and  $2\frac{3}{8}$  in. in inside depth, the bottom  $\frac{1}{2}$  in. of which shall be rounded. The pestle shall be 6 in. in length,  $1\frac{1}{2}$  in. in diameter, and rounded at the bottom. The upper part of the pestle should be slightly softer than the remainder in order to decrease the tendency to shatter. Both the mortar and pestle, after hardening, shall be polished with abrasive paper to remove all scale. The narrow clearance between the pestle and the sides of the mortar reduces the dust loss.

Mechanically operated pulverizing equipment may be substituted for the mortar and pestle, provided suitable tests show that the use of such equipment does not affect the composition of a sample of any material obtained by these methods.

NOTE 2.—For example, steel mortars and pestles of the following composition, after proper hardening and tempering treatments, have been found satisfactory:

Carbon, per cent. ....	0.60
Manganese, per cent. ....	0.25
Phosphorus, per cent. ....	0.02
Sulfur, per cent. ....	0.02
Silicon, per cent. ....	0.25
Chromium, per cent. ....	1.25
Tungsten, per cent. ....	2.20
Vanadium, per cent. ....	0.10

After machining annealed steel of this grade to the usual form and dimensions, each part is heated to between 760° and 800°C., quenched in a light mineral quenching oil, and tempered at once. The pestle may be treated by quenching the lower portion only, the upper portion being permitted to air cool, and then tempering the quenched portion.

(e) Sieves.—The sieves shall conform to the Specifications for Sieves for Testing Purposes (ASTM Designation: E11).<sup>3</sup>

*Unit Quantities for Sampling and Analysis.*—(a) Each shipment, except as otherwise agreed upon by the purchaser and the manufacturer, shall constitute a unit for sampling and analysis. It is recommended that shipments of any alloy exceeding 100 tons be divided into smaller lots for sampling according to some plan best adapted to the material and conditions, such as each cast, each carload, each ladleful, or each binful.

(b) Division of Samples.—In these methods the term "divide" is used to indicate a division of a sample into two approximately equal parts of similar composition as in riffing.

*Sampling. 1. Spiegeleisen and 15% Ferrosilicon.*—(a) Spiegeleisen is generally cast in pigs and shipped in bulk. Since this alloy is very hard and somewhat tough, sampling is most accurately and easily accomplished during the tapping of the metal from the furnace or during the pig-casting operation, by taking small spoonfuls and pouring the metal quickly into a test mold designed to solidify the metal quickly and give a clean test pig that is easily broken. Sampling of the metal in the solid state is difficult, and is best done during the loading or unloading, except when the material is loaded from bins or unloaded by dumping. The procedure,

<sup>3</sup> 1960 Supplement to Book of ASTM Standards, Parts 3 to 5 and 7 to 10.

therefore, may be varied to suit the conditions but shall always conform to the requirements set forth in the following paragraphs.

(b) **Sampling at Furnace.**—The purchaser may arrange with the manufacturer to have the sampling done at the furnace. If so, each shipment or each cast may constitute a unit sample for analyzing. The sample shall be obtained by collecting portions with a spoon from the runner as the metal flows from the furnace, unless the metal is treated in the runner or ladle to change its composition, in which event the portions shall be taken as the metal flows from the ladle to the pig casting machine. In any case, at least two spoonfuls of metal shall be taken from each ladle, one spoonful while the first third of a ladleful is flowing into or from the ladle, and the second while the last third is flowing. Each spoonful shall be taken in a manner that avoids collecting dirt or slag, and the clean metal shall be immediately poured into a clean shallow mold to form a thin chill casting from which small pieces, approximately equal in size, may be readily broken. When the spiegeleisen is cast in sand beds, the molten metal being run from the furnace directly to the casting floor, the samples shall be taken by dipping skimmed molten metal from the runner trough and pouring it into a small quartered cast-iron button mold. A sample shall be taken in this manner to represent the metal being cast in each pig bed. From the test castings thus obtained to represent a shipment, approximately equal portions shall be taken and combined to form the sample, which shall have a gross weight of not less than 200 g. The sample shall then be alternately crushed in a mortar, and sieved until it all passes through a No. 80 (177- $\mu$ ) sieve. If the sample is to be analyzed by more than one laboratory, it shall be mixed, coned, and quartered upon glazed paper (NOTE 3). The sample or samples thus prepared shall be thoroughly mixed, dried for 1 hr. at 105° to 110°C., and preserved for analysis in well-stoppered bottles properly labeled for full identification, including the name of the material, the manufacturer, the date, the cast or lot number, etc.

NOTE 3—Finished samples are frequently divided into four portions: one for the purchaser; one for the manufacturer; one for an umpire if necessary; and one held in reserve.

(c) **Sampling Solid Forms.**—When the metal is in the solid state a gross sample shall first be collected by selecting random pigs or pieces at regular intervals during the loading or unloading. Surface sampling of piles of the material will not give a representative sample. When piles of the material must be sampled, the pieces shall be selected according to some fixed plan which assures the obtaining of pieces comprising the gross sample from uniformly distributed points throughout, a condition requiring the moving of all or many of the pieces in the pile. For lots of 50 tons or larger, 1 pig or piece shall be taken for each ton, and for small lots the number of pieces shall be proportionately increased to 25 pieces for a 10-ton lot, or 10 pieces for a 1-ton lot.

The various pigs thus collected shall be broken approximately in half by any convenient means, and one of the halves of each pig shall be reserved. From the fractured surface of each of these half pigs, an approximately equal portion shall be taken by any suitable means (as by spalling with a heavy hammer), care being taken by the sampler to see that these spalls are not all from the outer edges of the pigs but at least some are obtained from the central portion, and that none contains portions of the outer surface which may be contaminated with sand or other foreign material. The spallings from each half pig as collected shall be placed in

separate envelopes and weighed to the nearest 1 g. Each portion so selected shall be of approximately the same weight.

The portions shall then be combined to form the sample, which shall be alternately crushed (preferably in a hardened-alloy steel mortar) and sieved until it passes a No. 6 (3360- $\mu$ ) sieve. Between 10 and 15 oz. shall then be separated from the crushed sample by riffing and this portion shall be pulverized to pass a No. 80 (177- $\mu$ ) sieve. The pulverizing of oversizes is best done with the hardened steel mortar and pestle, while sieving frequently to keep the size close to 177  $\mu$  and prevent loss of dust. The pulverized sample shall be thoroughly mixed upon glazed paper, divided if necessary, labeled, and dried prior to analysis, as described in Paragraph (b).

**2. Ferrosilicon, Standard Ferromanganese, Silicomanganese, Ferrophosphorus, and 12 to 15% Zirconium Alloy.**—(a) Alloys in this group are shipped in both lump and crushed form, in bulk as well as in containers. Carload lots are generally shipped in bulk, except the finely crushed sizes, which are usually shipped in containers. Different procedures are required for sampling the lump and the crushed alloy, and the work of sampling is most conveniently done while loading or unloading.

(b) **Lump Alloy.**—In sampling bulk shipments, lumps of average size shall be set aside for the sample at regular intervals in the ratio of one lump from approximately each 300 lb. The sample shall be accumulated throughout the loading or unloading operation so that all parts of the shipment will be equally represented. If the alloy is in containers, every fifth container shall be dumped, and one representative lump shall be taken from each 60 lb. of alloy which is equivalent to one lump per 300 lb. for the lot. The sample shall also include a representative amount of edge metal, small lumps, and any fines that may be present. From each of the lumps in the sample there shall be broken three small pieces each about  $\frac{3}{4}$  in. in size, one from each of two opposite surfaces (top and bottom, if present) and one from the center, the three pieces constituting a partial vertical cross-section of the lump.

The small pieces, together with a representative portion of any fines present, shall be combined and crushed to pass  $\frac{3}{4}$ -in. sieve. Not less than 30 lb. shall be separated from the crushed sample by riffing and at least a quarter portion of this shall be rolled to pass a No. 10 (2000- $\mu$ ) sieve. A 6- to 8-oz. portion obtained by riffing (a larger amount when more than one sample is required) of the 2000- $\mu$  sample shall then be pulverized to pass a No. 100 (149- $\mu$ ) sieve. The pulverizing is best done with the hardened alloy-steel mortar and pestle, while sieving frequently to keep the size close to 149  $\mu$ , and prevent loss of dust. The pulverized sample shall be poured upon glazed paper, mixed thoroughly, and divided, if necessary. (NOTE 3) by quartering, dried for 1 hr. at 105° to 110°C., and then preserved in a well-stoppered bottle or bottles.

(c) **Crushed Alloy.**—One container out of every 5 in the shipment shall be opened and the contents dumped. A sample representative of both lumps and fines shall be taken from each of the dumped containers to give a combined sample of approximately 1% of the weight of the lot or shipment, this sample being composed of equal amounts of the samples taken from all containers dumped. If in bulk, a fixed portion of representative material shall be taken with a shovel or scoop at regular intervals during the loading or unloading to accumulate a sample of about 1% of the weight of the lot.

The 1% sample shall be mixed and divided once if its weight is between 200 and

300 lb. or twice if it weighs more than 300 lb. The portion reserved shall be crushed to pass a 1-in. sieve (unless its largest pieces are under this size), again divided, and then crushed to pass a  $\frac{1}{4}$ -in. sieve. Preparation of the sample shall then be completed as described for  $\frac{1}{4}$ -in. material in Paragraph (b).

**3. High-Carbon Ferrochromium, Medium-Carbon Ferromanganese, Low-Carbon Ferromanganese, Silicon Metal, Calcium-Silicon, and 35 to 10% Zirconium Alloy.**—

(a) These alloys are shipped in both lump and crushed form, usually in containers.

(b) **Lump Alloy.**—One out of every 5 containers shall be dumped. Pieces  $\frac{1}{2}$  to  $\frac{3}{4}$  in. in size shall be broken from the lumps, and a fair proportion of any fines that may be present shall be included. The gross sample shall contain approximately one piece for each 50 lb. of alloy. The accumulated sample shall be mixed and reduced in size as described in the preceding section (b).

(c) **Crushed Alloy.**—Crushed alloy (material 2 in. and less in size) shall be sampled as described in the preceding section (c), except that a 10% representative sample shall be taken from each container opened to give a 2% gross sample. For lots of 10 tons or more, the 2% sample shall be mixed and divided once in half. For lots of less than 10 tons, dividing the sample at this stage shall be omitted. The portion retained shall be crushed to pass a 1-in. sieve (if above this size) in a heavy crusher provided with smooth plates of manganese steel, and again passed through the riffle to obtain a sample of about 100 lb. This portion shall be crushed to pass a  $\frac{1}{4}$ -in. sieve, divided twice, and the quarter portion reserved shall be crushed to pass a No. 10 (2000- $\mu$ ) sieve. Between 6 and 8 oz. shall then be separated from the crushed sample by riffing, and this portion shall be prepared for analysis as described in the preceding section (b).

For lots larger than 10 tons, a somewhat smaller percentage of the lump shall be crushed for the sample, while for smaller lots the percentage shall be increased somewhat to provide a suitable amount of sample for mixing and riffing to size.

**4. Low-Carbon Ferrochromium.**—(a) Low-carbon ferrochromium is shipped in both crushed and lump form, in bulk and in containers. The alloy usually contains about 70% chromium, and has a carbon content ranging from 0.06 to 2.0%, according to the maximum specified. The combination of hardness and toughness characteristic of this material, particularly of the lower carbon grades, makes it the most difficult of any of the ferro-alloys to sample properly. In view of the great importance of the accurate determination of the carbon content, the utmost care shall be taken to avoid contamination of the sample with fragments of steel from the tools used in preparing the sample. Bucking boards shall not be used.

(b) When the alloy is in lump form, a piece or pieces representing a full cross-section of the original cast shall be taken from points distributed throughout the lot, to give a gross sample amounting to about 1% of the weight of the lot. The cross-section pieces should be as nearly uniform in size as possible.

(c) When the alloy is in crushed form in containers, 1 container out of each 5 shall be emptied and sufficient representative material taken from each to give a gross sample of about 1% of the weight of the lot. For shipments in bulk, representative portions shall be selected with a shovel at regular intervals during the unloading operation to accumulate a 1% sample.

(d) The 1% sample shall be crushed to pass a 1-in. sieve (if above this size) in a heavy crusher provided with smooth plates of manganese steel, and riffled twice. The resulting quarter shall be crushed to pass a  $\frac{1}{2}$ -in. sieve and riffled once. The sample shall be further crushed to pass a  $\frac{1}{4}$ -in. sieve and riffled three times. The

resulting eighth portion of the sample shall be reduced to pass a No. 6 (3360- $\mu$ ) sieve by pounding in a hardened alloy-steel mortar, and riffled to a weight of 6 to 8 oz. This amount shall be pulverized to pass a No. 30 (590- $\mu$ ) sieve in a hardened alloy-steel mortar, while sieving frequently in order to keep the sample as near to this size as possible, until the entire sample has passed the sieve. The pulverized sample shall be mixed thoroughly upon glazed paper, divided if necessary (NOTE 3) by quartering, dried for 1 hr. at 105° to 110° C., and preserved in a well-stoppered bottle or bottles.

**5. Ferrovandium, Ferromolybdenum, Ferrotungsten, Ferromniobium, Ferrotitanium, Ferrozirconium, and Ferroboron.**—(a) These alloys are shipped in containers, and are all high-priced materials. Therefore, it is important that the sampling be thoroughly representative, irrespective of the amount of material involved.

(b) Shipments 20,000 lb. or Under in Weight.—All the containers of a shipment shall be emptied to form a cone-shaped pile. The pile shall be sampled by shoveling, the weight of the gross sample being adjusted to the size of the lumps of the alloy. For lots of more than 8000 lb., 1 shovelful out of every 4 shall be reserved for the sample. If the lot weighs less than 8000 lb., 1 shovelful out of 3 or out of 2, or shovelfuls otherwise adjusted so as to obtain a gross sample larger than the amounts specified below, shall be taken. The gross sample thus collected shall be coned and again divided by shoveling. This procedure shall be repeated, if necessary, until the weight of the gross sample is reduced to 2000 lb. for 2½-in. material, 250 lb. for 1-in. pieces, or 100 lb. for alloy crushed to ¼-in. size. In the case of ½-in. material the sample shall then be mixed and riffled once to 50 lb., but larger samples shall be crushed and divided as follows:

(1) *Coarse Material, 2½ in. Maximum.*—The 2000-lb. sample shall be crushed in a heavy crusher provided with smooth plates of manganese steel to pass through a 1-in. sieve, mixed thoroughly by coning at least three times, and riffled to 250 lb.

(2) *One-Inch Material.*—The 250-lb. sample shall be crushed in a heavy crusher provided with plates of manganese steel to pass a ½-in. sieve. After having been mixed thoroughly by coning at least 3 times, it shall be riffled to about 50 lb.

(3) *One-Fourth-Inch Material.*—The 50-lb. sample of ¼-in. material obtained in mixing and reduction of gross samples of 2½-in. or 1-in. material, or in splitting the gross sample of ½-in. material, shall be further crushed in laboratory rolls to pass a No. 10 (2000- $\mu$ ) sieve, again mixed thoroughly by coning, and riffled to 10 or 15 lb. This sample shall be crushed to pass a No. 20 (840- $\mu$ ) sieve, mixed thoroughly by coning, and divided with a riffle to 1 lb. or 500 g. The 500-g. sample shall be mixed thoroughly by coning and divided by riffling into four portions of about 125 g. each. Three of these portions shall be held in reserve, and one portion shall be pulverized in the hardened alloy-steel mortar to sizes retained between the No. 80 and No. 100 sieves (177- and 149- $\mu$ ). The pulverized sample shall be dried for 1 hr. at 105° to 110° C., poured upon glazed paper, mixed thoroughly, divided, if necessary (NOTE 3), by quartering and then preserved in a well-stoppered bottle or bottles.

(c) Shipments over 20,000 lb. in Weight.—When the shipment exceeds 20,000 lb., it shall be divided as nearly as possible into lots of 20,000 lb. each or fraction thereof, and the resulting 1-lb. or 500-g. samples taken shall be combined and mixed thoroughly by coning at least 3 times. This sample shall then be divided by riffling to 1 lb. or 500 g., which weight shall be further divided and pulverized as described in the preceding section (b) (2).

## WATER, REAGENTS, AND GLASSWARE

See Chapter 24.

## FERROSILICON

## SILICON BY THE SODIUM PEROXIDE FUSION METHOD

*Apparatus.* Iron Crucible.—A 30- or 50-ml. iron crucible will be required. A crucible made from No. 20 gauge ingot iron, 0.038 in. in thickness, will be suitable.

*Reagents.* Sulfurous Acid (6%).

*Procedure.*—(a) Transfer 0.5 g. of the sample of ferrosilicon (50 to 65% silicon) to a 30- or 50-ml. iron crucible, and add about 8 g. of dry  $\text{Na}_2\text{O}_2$ .<sup>4</sup> Mix thoroughly, using a platinum or iron rod, and carefully clean the rod of adhering particles by scraping with another rod. For grades of ferrosilicon containing 75% silicon and over (including silicon metals), mix 0.5 g. of the sample with about 8 g. of dry  $\text{Na}_2\text{O}_2$  and 2 to 4 g. of  $\text{Na}_2\text{CO}_3$ .

(b) Cover the mixture with a layer of about 2 g. of  $\text{Na}_2\text{O}_2$ . Heat the crucible and contents on a hot plate for 15 to 20 min. to expel any water in the  $\text{Na}_2\text{O}_2$  that would cause spattering in the subsequent fusion. Carefully fuse over a low flame by holding the crucible with a pair of tongs and slowly revolving it around the outer edge of the flame until the contents have melted down quietly. When the fusion is molten, rotate the crucible carefully to stir up any unattacked particles on the bottom or sides, the crucible and contents being maintained at a low red heat. Just before completion of the fusion, which requires only 3 or 4 min., increase the temperature to bright redness for 1 min. If the reaction proceeds violently with spattering of the contents, because of too rapid heating, the use of insufficient  $\text{Na}_2\text{O}_2$ , or the lack of thorough mixing, appreciable loss will occur and the work should be repeated.

(c) Cover the crucible, allow to cool almost to room temperature, and tap on an iron plate or solid object to loosen the fused mass in a cake. Transfer the cold cake to a dry 275-ml. platinum dish,<sup>5</sup> cover with a tight-fitting platinum lid, and cautiously add 50 ml. of cold water. When the reaction ceases, wash any small amount of material adhering to the crucible into the dish with a little water. Cool the solution and add 25 ml. of  $\text{H}_2\text{SO}_4$  (6%) to prevent attack on the dish by chlorine on acidifying with HCl. Cool, and carefully add HCl until in moderate excess.<sup>6</sup> Evaporate to dryness, preferably on a steam bath, but do not heat above 110°C. (An infrared lamp may be used.)

(d) When the residue is dry, allow the dish to cool. Add 20 ml. of HCl, stir well, cover the dish, and heat gently for a few minutes. Dilute with 200 ml. of hot

<sup>4</sup> Crucibles made from pure ingot iron contain only traces of silicon, and the amount of  $\text{SiO}_2$  present in the  $\text{Na}_2\text{O}_2$  used is usually negligible, but blanks should be run on new lots of crucibles and of  $\text{Na}_2\text{O}_2$ .

<sup>5</sup> If platinum dishes are not available for solution of the fused cake, it may be disintegrated with water in a pure nickel dish and the contents then transferred to a porcelain dish (of good glaze) containing sufficient HCl to provide an excess of acid. It is not desirable to dissolve the fusion directly in porcelain because of the action of the alkaline solution. If porcelain or pyrex must be used, it is necessary to carry along duplicate blanks.

<sup>6</sup> The use of  $\text{HClO}_4$  is not recommended for the dehydration of the silica in the fused sample since 100 to 125 ml. are necessary, and since it is exceedingly difficult to remove the  $\text{HClO}_4$  from the large amount of  $\text{SiO}_2$ , causing explosions during ignition.

water, digest for a few minutes, and filter through an 11-cm. paper containing a small amount of ashless paper pulp. Wash about 8 times with hot HCl (5:95) and then thoroughly with hot water. Reserve the paper and residue.

(e) Evaporate the filtrate to dryness, and bake the covered casserole or dish at 110°C. for 1 hr. Heating at a higher temperature is unnecessary and undesirable. Cool, add 20 ml. of HCl, and digest on a steam bath for 10 min. Add 200 ml. of warm water, stir well, filter immediately, and wash about eight times with hot HCl (5:95) and then thoroughly with hot water until free of chlorides.

(f) Place the papers and residues (Paragraphs (d) and (e)) in a 50-ml. platinum crucible and heat for 15 to 30 min. at approximately 200°C. Partially cover the crucible, and heat at from 500 to 600°C., until the paper is well charred without flaming. Gradually increase the temperature until the carbon is completely oxidized. Great care should be exercised in igniting the papers, as the current of air produced by a burning filter paper is sufficient to carry finely divided  $\text{SiO}_2$  out of the crucible. Cover the crucible tightly and heat to the full heat of the blast lamp, or in a muffle furnace, at a temperature of 1100° to 1150°C. for 25 min. Cool in a desiccator, weigh, and again ignite for 10 min. at the same temperature, as a check for constant weight.

(g) Add sufficient  $\text{H}_2\text{SO}_4$  (1:1) to moisten the residue and then add 5 to 8 ml. of HF. Evaporate to dryness, ignite at 1000°C., and weigh. The loss in weight represents  $\text{SiO}_2$ .

(h) Blank.—Make a blank determination, following the same procedure and using the same amounts of all reagents.

(i) Calculation.—Calculate the percentage of silicon as follows: <sup>7</sup>

$$\text{Silicon, per cent} = \frac{(A - B) \times 0.4672}{C} \times 100$$

where  $A$  = grains of  $\text{SiO}_2$ ,

$B$  = correction for blank, in grams, and

$C$  = grams of sample used.

## TOTAL CARBON BY THE DIRECT-COMBUSTION METHOD

**Apparatus.** Apparatus for Determination of Total Carbon by Direct Combustion.—See Chapter 24, p. 654.

**Procedure.**—(a) Mix 2 g. of the sample with 2 g. of powdered CuO and transfer the mixture to a combustion boat made of zirconium oxide-base refractory (having inside dimensions 100 mm. in length, 13 mm. in width, and 8 mm. in depth) or equivalent, provided with a bed of 90-mesh crystalline aluminum oxide molded in the form of a trench. Cover the mixture with 2 g. of 40-mesh ingot-iron drillings or millings. Cover the sample with a suitable cover and introduce the boat into the hot combustion tube. Close the tube and allow the sample to heat for 1 to 2 min.<sup>8</sup> Then admit the oxygen at a rate of 800 to 1000 ml. per min. while combustion is

<sup>7</sup> For the recommended procedure for rounding off calculated values, see Section 3 (d) to (h) of the Recommended Practices for Designating Significant Places in Specified Limiting Values (ASTM Designation: E29), 1960 Book of ASTM Methods for Chemical Analysis of Metals.

<sup>8</sup> If the sample is allowed to come to the temperature of the furnace before the oxygen is admitted, it usually bursts into a bright flame and burns completely. A period of 1 to 2 min. of preheating suffices.

going on.<sup>9</sup> Use a furnace temperature of 1200° to 1350°C. When combustion is complete (1.5 to 2 min.), continue the flow of oxygen for 6 to 8 min. in order to sweep out the CO<sub>2</sub>.

(b) Withdraw the absorption tube filled with oxygen, place it in the balance case for 10 min.,<sup>10</sup> open momentarily, and weigh against a similar tube used as a counterpoise. The increase in weight represents CO<sub>2</sub>.

(c) Remove the boat from the tube and examine the melt for evidences of incomplete combustion. If the sample is not thoroughly fused in a solid pig, the determination shall be rejected.

(d) Blank.—Make a blank determination, following the same procedure and using the same amounts of all materials except the sample.

(e) Calculation.—Calculate the percentage of carbon as follows:

$$\text{Carbon, per cent} = \frac{(A - B) \times 0.2729}{C} \times 100$$

where *A* = grams of CO<sub>2</sub>,

*B* = correction for blank, in grams, and

*C* = grams of sample used.

### PHOSPHORUS BY THE PERCHLORIC ACID-ALKALIMETRIC METHOD

**Reagents.** (a) Perchloric Acid (70%).

(b) Potassium Permanganate Solution (25 g. per liter).

(c) Ammonium Molybdate Solution (Acidic).

**Solution No. 1.**—Mix thoroughly 100 g. of molybdic acid (85% MoO<sub>3</sub>) and 240 ml. of water. Add 140 ml. of NH<sub>4</sub>OH, while stirring vigorously. When solution is complete, filter, and add 60 ml. of HNO<sub>3</sub>.

**Solution No. 2.**—Mix 400 ml. of HNO<sub>3</sub> and 960 ml. of water.

When the solutions are cool, add Solution No. 1 to Solution No. 2, while stirring constantly. Add 0.1 g. of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, and allow the solution to stand at least 24 hr. before using. Use only the clear supernatant solution.

(d) Standard Sodium Hydroxide Solution (1 ml. = 0.0002 g. P, approximately 0.15 N).

**Preparation.**—Dissolve 75 g. of NaOH in 75 ml. of water, and transfer to a large test tube, taking care not to wet the top. Stopper tightly, and let stand in a vertical position until the supernatant liquid is clear. Carefully withdraw about 5 ml. of the clear liquid with a pipet and run it into 1 liter of freshly boiled and cooled water. Mix well and store away from contact with the air.

**Standardization.**—Dissolve 0.4000 g. of the National Bureau of Standards stand-

<sup>9</sup> The rate at which oxygen is admitted is also a factor in the velocity of combustion. Assuming the combustion apparatus has been heated to the temperature range above that recommended, it is possible, if the material is closely packed and if oxygen is admitted at too rapid a rate, that the combustion may be so violent as to cause excessive spattering of fused oxides and such fluidity of the molten slag that the boat or other container may be injured or destroyed. Sufficient oxygen, however, shall be run in to ensure a current of gas through the absorber at all stages of the combustion.

<sup>10</sup> The tube will warm up when CO<sub>2</sub> is absorbed. It is not necessary to wait until it reaches room temperature if it is in continuous use, provided the same time interval is maintained and approximately the same amount of CO<sub>2</sub> is absorbed.



ard sample of potassium acid phthalate in 100 ml. of freshly boiled and cooled water. Add 3 drops of an alcoholic solution of phenolphthalein (2 g. per liter) and titrate to a faint pink color with the NaOH solution.

Where empirical standardization against phosphorus is required, directions will be found in the methods concerned.

Calculate the phosphorus equivalent by using the ratio 23 NaOH to 1 phosphorus. One milliliter of 1 N NaOH is equivalent to 0.00135 g. of phosphorus. The solution may also be standardized against National Bureau of Standards standard steels. Protect the NaOH solution from  $\text{CO}_2$  by means of a soda-lime or soda-asbestos tube.

(e) Phenolphthalein Indicator Solution (10 g. per liter).

(f) Standard Nitric Acid.—Dilute 10 ml. of clear  $\text{HNO}_3$  to 1 liter with water, and standardize against the standard NaOH solution, using phenolphthalein as the indicator. If desired, the  $\text{HNO}_3$  may be rendered equivalent to the NaOH solution by dilution with water.

*Procedure.*—(a) Transfer 2 g. of the sample to a 300-ml. platinum dish provided with a platinum cover, and add 25 ml. of  $\text{HNO}_3$ . Add HF cautiously, a few drops at a time, until complete decomposition of the alloy is effected and a total of 15 ml. of HF has been added. Remove the cover and rinse it with a jet of water. Add 15 ml. of  $\text{HClO}_4$  (70%), and heat on a sand bath to dense white fumes. Rinse down the sides of the dish with a little water and again heat to dense white fumes; then continue the heating for 5 min. longer.

(b) Cool, add 50 ml. of water, and transfer to a 300-ml. Erlenmeyer flask. Boil for several minutes to expel free chlorine; then add 2 ml. of  $\text{HNO}_3$  and an excess of  $\text{KMnO}_4$  (25 g. per liter). Boil for several minutes, and then destroy the excess  $\text{KMnO}_4$  by the addition, drop by drop, of a saturated solution of  $\text{Na}_2\text{SO}_3$  or  $\text{H}_2\text{SO}_3$ .

(c) Boil for a few minutes longer to expel oxides of nitrogen, and cool to room temperature. Add 10 g. of  $\text{NH}_4\text{NO}_3$ , 0.05 g. of ferrous ammonium sulfate dissolved in 10 ml. of water, and 50 ml. of ammonium molybdate solution. Stopper the flask and shake vigorously for 5 min.

(d) Allow to settle for 10 min.; if the alloy contains less than 0.02% of phosphorus, allow to stand 30 min. Filter and wash six or eight times with cold  $\text{HNO}_3$  (1:99),<sup>11</sup> and finally 12 to 15 times (or until free of acid) with  $\text{KNO}_3$  (10 g. per liter).

(e) Return the precipitate and paper to the precipitating vessel. Add 1 to 3 ml. in excess of NaOH (1 ml. = 0.0002 g. P) and 25 ml. of water, both free of  $\text{CO}_2$ , and shake or stir until the precipitate is dissolved. Dilute to 100 ml. with water free of  $\text{CO}_2$ , add 3 drops of phenolphthalein indicator solution and discharge the pink color with standard  $\text{HNO}_3$ . Finish the titration by adding NaOH (1 ml. = 0.0002 g. P) to the reappearance of the pink color.

(f) Blank.—Make a blank determination, following the same procedure and using the same amounts of all reagents.

(g) Calculation.—Calculate the percentage of phosphorus as follows:

$$\text{Phosphorus, per cent} = \frac{[(A - BC) - (D - EC)]F}{G} \times 100$$

<sup>11</sup> If desired, the determination may be completed by the molybdate-magnesia method as described in Chapter 24.

where  $A$  = milliliters of NaOH solution required by the sample (Paragraph (e)),  
 $B$  = milliliters of  $\text{HNO}_3$  required by the sample (Paragraph (e)),  
 $C$  = milliliters of NaOH solution equivalent to 1 ml. of the  $\text{HNO}_3$ ,  
 $D$  = milliliters of NaOH required by the blank (Paragraph (f)),  
 $E$  = milliliters of  $\text{HNO}_3$  required by the blank (Paragraph (f)),  
 $F$  = phosphorus equivalent of the NaOH solution, in grams per milliliter, and  
 $G$  = grams of sample used.

### SULFUR BY THE NITRIC-HYDROFLUORIC ACID-GRAVIMETRIC METHOD

**Reagents.** (a) Perchloric Acid (70%).

(b) Zinc (20-mesh).

(c) Barium Chloride Solution (100 g. per liter).

(d) Barium Chloride Wash Solution.—Add 5 ml. of HCl to 100 ml. of  $\text{BaCl}_2$  (100 g. per liter) and dilute to 1 liter.

**Procedure.**—(a) Transfer 5 g. of the sample to a 300-ml. platinum dish equipped with a platinum cover, and add 150 ml. of  $\text{HNO}_3$ . Add 1 to 2 ml. of HF. Heat, if necessary, to start the reaction. Remove the dish from the source of heat and add cautiously several milliliters of HF. Repeat the procedure until the sample is dissolved. From 50 to 60 ml. of HF are required. Add 1 g. of  $\text{Na}_2\text{CO}_3$ . Remove the cover and rinse it with water. Add 30 ml. of  $\text{HClO}_4$  (70%), rinse down the sides of the dish with a little water, evaporate the solution to dense white fumes, and continue heating until the volume has been reduced to approximately 20 ml. Cool, add 20 ml. of water, and repeat the evaporation to dense white fumes.

(b) Cool, add 25 ml. of water and 0.1 g. of boric acid, digest, and transfer to a 250-ml. beaker. Boil for 3 to 5 min. to expel free chlorine. Dilute to 50 ml., add 10 ml. of HCl and 5 g. of 20-mesh zinc, and warm on a steam bath until the iron is reduced to the ferrous state and the evolution of hydrogen has nearly ceased. Filter through a 9-cm. close-texture paper, wash the paper 12 to 15 times with hot HCl (1:99), and discard.

(c) Warm the filtrate to 60° to 70°C., and add 10 ml. of  $\text{BaCl}_2$  (100 g. per liter). Stir vigorously and let stand for 18 to 24 hr. Filter on a 9-cm. close-texture paper, wash 10 to 12 times with  $\text{BaCl}_2$  wash solution, and then wash 15 to 18 times with HCl (1:99).<sup>12</sup>

(d) Ignite in platinum, first at a low temperature and finally at approximately 900°C. Cool, and weigh as  $\text{BaSO}_4$ .

(e) Blank.—Make a blank determination following the same procedure and using the same amounts of all reagents.

(f) Calculation.—Calculate the percentage of sulfur as follows:

$$\text{Sulfur, per cent} = \frac{(A - B) \times 0.1374}{C} \times 100$$

where  $A$  = grams of  $\text{BaSO}_4$ ,

$B$  = correction for blank, in grams, and

$C$  = grams of sample used.

<sup>12</sup> If desired, the washings may be kept separate and examined for  $\text{BaSO}_4$  as follows: evaporate the washings to dryness; dissolve the slight residue in 50 ml. of hot HCl (2:98); add 2 ml. of  $\text{BaCl}_2$  (100 g. per liter); and digest at 70° to 80°C. for 2 hr., avoiding any undue evaporation; filter on a small close-texture paper; wash 3 times with cold HCl (1:99), and 10 times with warm water. The recovery of  $\text{BaSO}_4$  that is ordinarily obtained represents approximately 0.001 to 0.002% of sulfur.

## FERROMANGANESE, SILICOMANGANESE, AND MANGANESE-SILICON

## MANGANESE

THE BISMUTHATE METHOD<sup>13</sup>

**Apparatus.** Filter.—Digest a suitable grade of asbestos in hot  $\text{HNO}_3$  and then wash it free of acid with hot water. Prepare a pad of the asbestos on a 2-in. aluminum or perforated porcelain plate resting in a large glass funnel.

**Reagents.** (a) Perchloric Acid (70%).

(b) Standard Sodium Thiosulfate Solution (0.1 N).

**Preparation.**—Dissolve 24.8 g. of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in 1 liter of freshly boiled and cooled water in a sterile glass bottle. If sulfur precipitates during preparation or upon subsequent use, discard the solution and prepare a new one.

**Standardization.**—Pipet 25 ml. of 0.1 N  $\text{KIO}_3$  into a 125-ml. flask. Add 30 ml. of water, 1 g. of KI, and 10 ml. of  $\text{H}_2\text{SO}_4$  (1:1). Titrate with the  $\text{Na}_2\text{S}_2\text{O}_3$  solution to a light straw color. Add 2 ml. of starch solution (10 g. per liter) and continue titration to the disappearance of the blue color.

Where empirical standardization against copper is required, directions will be found in the methods concerned.

(c) Sodium Bismuthate.—This reagent shall be of the 80% grade and free of manganese. Test its oxidizing power as follows: shake 0.5 g. of  $\text{NaBiO}_3$  and 4 g. of KI with a little water in a stoppered flask; add 15 ml. of  $\text{HCl}$  and allow to stand in the dark, while shaking occasionally, until the  $\text{NaBiO}_3$  has entirely decomposed; dilute to 300 ml. and titrate with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ , using starch as an indicator at the end. One milliliter of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  is equivalent to 0.0110 g. of  $\text{NaBiO}_3$ .

To test for manganese, add 5 g. of  $\text{NaBiO}_3$  to 15 ml. of  $\text{HNO}_3$  (1:3). Heat and dissolve by adding drop by drop a dilute solution of  $\text{FeSO}_4$ . Continue as described below under the procedure for ferromanganese and manganese metal, to the addition of  $\text{NaBiO}_3$ , when the development of a pink color will show the presence of manganese.

(d) Nitric Acid (3:97).—Boil 40 ml. of  $\text{HNO}_3$  under the hood until decolorized, cool, and pass in a current of clean air for 5 min. Mix 30 ml. of this acid with 970 ml. of water. Add 1 g. of  $\text{NaBiO}_3$ , shake, and allow to settle. Use only the clear supernatant liquid.

(e) Ferrous Ammonium Sulfate.—Fine, well-mixed crystals of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  will be required. Determine the manganese equivalent as follows: transfer 2.0 g. of  $\text{NaBiO}_3$  to a 1-liter Erlenmeyer flask; add 250 ml. of cold  $\text{HNO}_3$  (1:3); and vigorously agitate the solution for 1 min.; dilute with 250 ml. of cold water, and immediately filter through a layer of acid-washed asbestos as described in the following section, Paragraph (b); add 100 ml. of 0.1 N  $\text{KMnO}_4$  to the filtrate; stir, add 5.000 g. of ferrous ammonium sulfate and a few drops of 0.01 M 1,10-phenanthroline indicator, and immediately titrate the excess of the ferrous salt with 0.1 N  $\text{KMnO}_4$  to a clear green color that persists for at least 30 sec.

(f) 1,10-Phenanthroline-Ferrous Complex Indicator Solution (0.025 M).

<sup>13</sup> This method is not applicable in the presence of cobalt, but this element is seldom encountered in ferromanganese.

Dissolve 1.485 g. of 1,10-phenanthroline monohydrate in 100 ml. of 0.025 *M* ferrous sulfate solution.

(g) **Standard Potassium Permanganate Solution (0.1 *N*).** *Preparation.*—Dissolve 3.2 g. of  $\text{KMnO}_4$  in 1 liter of water. Let stand in the dark for 2 weeks, and filter, without washing, through a Gooch crucible or a fritted-glass crucible of fine porosity, avoiding contact with rubber or other organic material. Store in a dark-colored, glass-stoppered bottle.

*Standardization.*<sup>14</sup>—Transfer 0.3000 g. of the National Bureau of Standards standard sample of sodium oxalate<sup>15</sup> dried at 105°C., to a 600-ml. beaker. Add 250 ml. of  $\text{H}_2\text{SO}_4$  (5:95), previously boiled for 10 to 15 min. and then cooled to 27° ± 3°C. Stir until the oxalate has dissolved. Add 39 to 40 ml.<sup>16</sup> of the  $\text{KMnO}_4$  solution at a rate of 25 to 35 ml. per min., while stirring slowly. Let stand until the pink color disappears (about 45 sec.).<sup>17</sup> Heat to 55° to 60°C., and complete the titration by adding the  $\text{KMnO}_4$  solution until a faint pink color persists for 30 sec. Add the last 0.5 to 1 ml. drop by drop, with particular care to allow each drop to become decolorized before the next is introduced.

Determine the amount of  $\text{KMnO}_4$  required to impart a faint pink color to the solution by adding the  $\text{KMnO}_4$  solution to the same volume of the boiled and cooled  $\text{H}_2\text{SO}_4$  (5:95) at 55° to 60°C. This correction usually amounts to 0.03 to 0.05 ml.

*Procedure. 1. Ferromanganese and Manganese Metal.* (a) **Solution of Sample.**—Transfer 0.25 g. of the sample to a 1-liter Erlenmeyer flask, and add 15 ml. of  $\text{HNO}_3$  (1:3). Heat cautiously until the sample is dissolved. Add 8 ml. of  $\text{HClO}_4$  (70%) and boil gently until the acid fumes strongly and  $\text{MnO}_2$  begins to separate.<sup>18</sup> The heat applied to the flask shall be such that the  $\text{HClO}_4$  refluxes down the sides, and no great amount is lost by volatilization. Cool, add 5 ml. of water and 25 ml. of  $\text{HNO}_3$  (1:3), and boil for several minutes to expel free chlorine. Add sufficient  $\text{H}_2\text{SO}_3$  or  $\text{NaNO}_2$  solution to just dissolve the separated  $\text{MnO}_2$ , and to reduce any chromic acid formed from any chromium in the alloy during fuming with  $\text{HClO}_4$ . Boil the solution for 3 min. to completely expel oxides of nitrogen. Cool to room temperature, add 225 ml. of colorless  $\text{HNO}_3$  (2:5) and sufficient water to bring the total volume to 250 ml., and cool to 10° to 15°C.

(b) **Oxidation of Manganese.**—If the directions in Paragraph (a) have been followed, the manganese will, at this point, be present in a concentration of approximately 0.001 g. per milliliter of  $\text{HNO}_3$  (1:3). This concentration of manganese

<sup>14</sup> Towler, R. M., and Bright, H. A., Standardization of Permanganate Solutions with Sodium Oxalate, *Journal of Research, Nat. Bureau Standards (Research Paper RPS49)*, 15, 5, 493, September, 1935.

<sup>15</sup> If the Bureau of Standards standard sample of sodium oxalate is unavailable, pure sodium oxalate may be prepared according to Sorensen by (a) two recrystallizations from water of the reagent grade substance, or (b) precipitation from an aqueous solution with alcohol. See Sodium Oxalate as a Standard in Volumetric Analysis, *Circular C40*, Nat. Bureau Standards, 5, 1913.

<sup>16</sup> A 0.3-g. portion of sodium oxalate requires 44.77 ml. of 0.1 *N*  $\text{KMnO}_4$ .

<sup>17</sup> If the pink color should persist because the  $\text{KMnO}_4$  is too strong, discard, and begin again, adding a few milliliters less of the  $\text{KMnO}_4$  solution.

<sup>18</sup> Chromium in amounts less than 2% does not cause appreciable interference if the oxidation and titration are rapidly done in cold solutions. Larger amounts interfere to some extent, and should be separated prior to the final oxidation with  $\text{NaBiO}_3$ . The separation is most conveniently made during the initial fuming with  $\text{HClO}_4$ , by adding small portions of  $\text{HCl}$  as soon as all the  $\text{HNO}_3$  has been expelled. After alternately adding  $\text{HCl}$  and fuming, add 5 ml. of  $\text{HClO}_4$ , and permit the fuming to continue as directed in the absence of chromium.

and  $\text{HNO}_3$ , and a temperature of  $10^\circ$  to  $15^\circ\text{C}$ ., are conditions necessary to insure maximum stability of the permanganic acid to be formed as further described. To ensure complete oxidation of the manganese to permanganic acid, it is essential that the  $\text{NaBiO}_3$  be used in the ratio of at least 26 g. to every gram of manganese in solution. Add approximately 7 g. (9 g. if the sample is manganese metal) of  $\text{NaBiO}_3$  to the flask, agitate briskly for 1 min., dilute with 250 ml. of cold water, and filter immediately through an asbestos pad (see Apparatus). The filter can be washed free from manganese more readily if not allowed to run dry during the filtering and washing. Wash the filter and residue with cold, freshly boiled  $\text{HNO}_3$  (3:97) until the washings are entirely colorless, and immediately treat the filtrate and washings as described in Paragraph (c).

(c) Add 9 g. (slightly more if the sample is manganese metal) of ferrous ammonium sulfate to the filtered solution of permanganic acid. Stir briskly. As soon as reduction is complete and all of the salt has dissolved, add a few drops of 0.01 *M* 1,10-phenanthroline indicator and titrate the excess ferrous ammonium sulfate with 0.1 *N*  $\text{KMnO}_4$  to a clear green color that persists for at least 30 sec.

(d) Calculation.—Calculate the percentage of manganese as follows:

$$\text{Manganese, per cent} = \frac{(A - B) \times 0.0110}{C} \times 100$$

where *A* = milliliters of exactly 1 *N*  $\text{KMnO}_4$  equivalent to grams of ferrous ammonium sulfate added,

*B* = milliliters of exactly 1 *N*  $\text{KMnO}_4$  required to titrate the excess ferrous ammonium sulfate, and

*C* = grams of sample used.

**2. Silicomanganese and Manganese-Silicon.** (a) *Solution of Sample.*—Transfer 0.3 g. of silicomanganese (60 to 70% manganese) or 1 g. of manganese-silicon (20 to 25% manganese) to a large platinum dish fitted with a platinum cover, and add 10 ml. of  $\text{HF}$ . (Some spiegeleisens are completely soluble in  $\text{HNO}_3$ , in which case the sample may be dissolved directly, as described in Section 1.) When the reaction moderates, add  $\text{HNO}_3$ , a few drops at a time, until the sample is dissolved. Remove the cover and rinse it with water. Add 8 ml. of  $\text{HClO}_4$  (70%) and evaporate to dense white fumes or until  $\text{MnO}_2$  begins to separate. Cool, transfer to a 1-liter Erlenmeyer flask, and boil for several minutes to expel free chlorine; next rinse the dish into the Erlenmeyer flask with 25 ml. of  $\text{HNO}_3$  (1:3) plus sufficient  $\text{H}_2\text{SO}_4$  to dissolve the separated  $\text{MnO}_2$ . Boil for 3 min. and cool. Add 225 ml. of colorless  $\text{HNO}_3$  (2:5) and sufficient water to bring the volume to 250 ml., and cool to  $10^\circ$  to  $15^\circ\text{C}$ .

(b) Complete the determination as described in Section 1 (b) to (d).

### THE PYROPHOSPHATE (POTENTIOMETRIC) METHOD (E31-60T)

*Scope.*—This method covers the determination of manganese in commercial grades of ferromanganese and silicomanganese in the range from 60 to 90%.

*Summary of Method.*—Manganous manganese, in a neutral pyrophosphate solution, is titrated potentiometrically with permanganate. The manganous ion is oxidized, and the permanganate reduced, to a trivalent pyrophosphate complex.

*Interferences.*—Provision has been made for removal of interfering elements.

*Apparatus.* (a) *pH Meter.*—This should be equipped with a platinum electrode, a fresh, sleeve-type, calomel-shielded electrode (Nore 4), and a glass electrode.

NOTE 4.—Calomel electrodes that have been allowed to dry out will give very poor results.

(b) **Magnetic Stirrer.**—Use of a tetrafluorethylene (Teflon) covered stirring bar is recommended.

**Reagents.** (a) Boric Acid ( $\text{H}_3\text{BO}_3$ ).

(b) **Hydrogen Peroxide (3%).**—Dilute 1 volume of concentrated hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%) with 9 volumes of water.

(c) **Potassium Permanganate, Standard Solution (0.05 N).**

(d) **Sodium Hydroxide Solution (200 g. per liter).**—Dissolve 200 g. of sodium hydroxide ( $\text{NaOH}$ ) in water and dilute to 1 liter. Prepare fresh as needed.

(e) **Sodium Pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) (NOTE 5).**

NOTE 5.—The sodium pyrophosphate must be free from impurities. Each lot should be tested by analyzing a solution containing a known amount of manganese in the form of a standard manganous solution. If the results are erratic, the sodium pyrophosphate should be purified by recrystallization.

**Procedure for Ferromanganese.**—(a) Transfer 0.2 g. of sample, weighed to the nearest 0.1 mg., to a 400-ml. beaker. Add 20 ml. of  $\text{HNO}_3$  (1:1), 10 ml. of  $\text{HClO}_4$ , and 8 to 10 drops of  $\text{HF}$ . Cover the beaker immediately, place on a hot plate, and digest until complete dissolution is effected and nitrogen oxide fumes have been expelled. Then add 1 g. of  $\text{H}_3\text{BO}_3$ , and evaporate to copious white fumes. Withdraw the cover slightly and volatilize any chromium present by the dropwise addition of  $\text{HCl}$ . When chromyl chloride has been expelled, as evidenced by the disappearance of the orange vapors, replace the cover and evaporate to copious white fumes. Cool, add 10 ml. of  $\text{HCl}$  (1:1) and 1 ml. of  $\text{H}_2\text{O}_2$ , and boil for 4 to 5 min.

(b) Cool to room temperature, wash down the cover and sides of the beaker, dilute to 150 to 200 ml., and add 35 g. of  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ . Place a stirring magnet in the beaker, place the beaker on a magnetic stirrer, and stir until the salt dissolves. Using a pH meter (with calomel and glass electrodes), adjust the solution to pH 6.5 with  $\text{NaOH}$ , and  $\text{HCl}$  if necessary. The solution should be clear. If a precipitate forms, dilute further and stir until a clear solution results, maintaining a pH of 6.5. Cool to  $20^\circ\text{C}$ . (NOTE 6).

NOTE 6.—Allowing the solution to stand for at least 5 min. and cooling to  $20^\circ\text{C}$ . before titration gives a more stable initial potential.

(c) Titrate potentiometrically with  $\text{KMnO}_4$  solution, using the pH meter equipped with platinum and calomel electrodes. Add the reagent rapidly until the first deflection of the galvanometer is noted and then dropwise to the equivalence point. The drop giving the largest potential change is taken as the end point.

**Procedure for Silicomanganese.**—Transfer 0.25 g. of silicomanganese, weighed to the nearest 0.1 mg., to a 400-ml. beaker. Add 20 ml. of  $\text{HNO}_3$  (1:1), 10 ml. of  $\text{HClO}_4$ , and 20 drops of  $\text{HF}$ . Proceed as above.

**Calculation.**—Calculate the percentage of manganese as follows:

$$\text{Manganese, per cent} = \frac{AB \times 0.04395}{C} \times 100$$

where  $A$  = milliliters of  $\text{KMnO}_4$  solution required for the titration,

$B$  = normality of the  $\text{KMnO}_4$  solution, and

$C$  = grams of sample used.

## TOTAL CARBON BY THE DIRECT-COMBUSTION METHOD

*Procedure.*—Determine carbon by the direct-combustion method described above under Ferrosilicon (p. 765), with the following modifications:

- (1) Use 0.25 to 0.50 g. of the sample.
- (2) Use a furnace temperature of 1200° to 1350°C.
- (3) When testing high-silicon material, mix the sample with 1 g. of powdered CuO and cover with 1 to 2 g. of 40-mesh ingot iron drillings or millings.

PHOSPHORUS BY THE PERCHLORIC ACID-  
ALKALIMETRIC METHOD

*Reagents.*—For descriptions of the reagents required, see the section on the procedure for determination of phosphorus, above.

*Procedure.*—(a) Dissolve 2 g. of the sample of ferromanganese in 50 ml. of  $\text{HNO}_3$ .

(b) In the case of silicomanganese or manganese-silicon, transfer 2 g. of the sample to a large platinum dish. Cover and add 50 ml. of  $\text{HNO}_3$ , and then from 10 to 15 ml. of HF in small amounts.

(c) When solution is complete (Paragraph (a) or (b)), add 20 ml. of  $\text{HClO}_4$  (70%), and evaporate to dense white fumes, or until  $\text{MnO}_2$  begins to separate. Take up in 50 ml. of water and sufficient  $\text{H}_2\text{SO}_4$  to dissolve the precipitated  $\text{MnO}_2$ , boil, and filter into a 300-ml. Erlenmeyer flask to remove  $\text{SiO}_2$ . Wash the paper and  $\text{SiO}_2$  well with  $\text{HNO}_3$  (1:99), ignite in platinum at a low heat, and add several milliliters of HF and 2 ml. of  $\text{HClO}_4$  (70%). Evaporate to dense white fumes, add to the main solution, boil for 2 to 3 min. and cool to room temperature.<sup>19</sup>

(d) To the cold solution (100 ml. in volume) add 2 ml. of  $\text{HNO}_3$  and 0.05 g. of phosphorus-free ferrous ammonium sulfate, and bring the temperature to 25°C.<sup>20</sup> Add 50 ml. of ammonium molybdate solution, stopper the flask, and shake vigorously for 5 min.

(e) Complete the determination as described in the section for phosphorus in ferrosilicon.

## SULFUR BY THE NITRIC ACID OXIDATION METHOD

*Reagents.* (a) Barium Chloride Solution (100 g. per l.).

(b) Zinc (20- to 30-mesh, sulfur-free).

*Procedure.*—(a) Dissolve 5 g. of the sample in 75 ml. of  $\text{HNO}_3$ . When solution is complete, add 0.5 g. of  $\text{Na}_2\text{CO}_3$ , and carefully evaporate to dryness in a sulfur-free atmosphere. Bake for 15 to 20 min. on a hot plate. Cool, add 30 ml. of HCl, and warm gently until salts are dissolved. Add 30 ml. of HCl and evaporate to sirupy consistency.

(b) Add 10 ml. of HCl, 25 ml. of water, and 5 g. of 20- to 30-mesh sulfur-free zinc, and warm on a steam bath until the iron is reduced to the ferrous state and the evolution of hydrogen has nearly ceased. Filter through a close-texture paper and wash with 75 ml. of HCl (1:99).

<sup>19</sup> If titanium is present, evaporate the  $\text{HClO}_4$ -HF solution of the  $\text{SiO}_2$  just to dryness. Fuse the residue with a small amount of  $\text{Na}_2\text{CO}_3$ , leach the melt with 25 ml. of water, cool, and filter. Make the filtrate just acid with  $\text{HNO}_3$  and add it to the main solution.

<sup>20</sup> If vanadium is present in amounts over 0.08%, reduce it with  $\text{FeSO}_4$  and  $\text{H}_2\text{SO}_4$  before precipitation with molybdate.

(c) Warm the filtrate to 60° to 70°C. and add 20 ml. of  $\text{BaCl}_2$  (100 g. per liter).<sup>21</sup> Stir vigorously and let stand 18 to 24 hr. Filter on a 9-cm. close-texture paper and discard the filtrate. Wash once or twice with cold  $\text{HCl}$  (1:500) and then with hot water until free of chlorides. Reserve the precipitate.

(d) Add 2 ml. of  $\text{BaCl}_2$  (100 g. per liter) to the washings and evaporate to dryness. To the residue, add 2 ml. of  $\text{HCl}$  (1:1) and 25 ml. of warm water, and digest at 60° to 70°C. for several hours. Filter on a small close-texture paper and wash with hot water until free of chlorides.<sup>22</sup>

(e) Ignite both papers (Paragraphs (c) and (d) in platinum. Add 1 drop of  $\text{H}_2\text{SO}_4$  (1:1) and 1 ml. of  $\text{HF}$ . Evaporate to dryness, ignite, and weigh as  $\text{BaSO}_4$ .

(f) Blank.—Make a blank determination, following the same procedure and using the same amounts of all reagents.

(g) Calculation.—Calculate the percentage of sulfur as follows:

$$\text{Sulfur, per cent} = \frac{(A - B) \times 0.1374}{C} \times 100$$

where  $A$  = grams of  $\text{BaSO}_4$ ,

$B$  = correction for blank, in grams, and

$C$  = grams of sample used.

### SILICON BY THE NITRIC-SULFURIC ACID METHOD

**Reagents.** Nitric-Sulfuric Acid Mixture.—Slowly stir 160 ml. of  $\text{H}_2\text{SO}_4$  into 660 ml. of water, and add 180 ml. of  $\text{HNO}_3$ .

**Procedure.** 1. *Ferromanganese and Manganese Metal.*—(a) Dissolve 1 g. of the sample with 50 ml. of the  $\text{HNO}_3$ - $\text{H}_2\text{SO}_4$  mixture in a 250-ml. porcelain casserole, and evaporate gently to dense white fumes.

(b) After the solution has cooled somewhat, add 125 ml. of water and 5 ml. of  $\text{HCl}$ . Heat, while stirring frequently, until all salts are dissolved, and immediately filter on a 9-cm. paper. Wash the precipitate with hot  $\text{HCl}$  (5:95) and hot water alternately, to complete the removal of soluble salts, and finally with hot water until free of acid.

(c) Transfer the paper and precipitate to a platinum crucible, char the paper carefully, cover the crucible, and ignite over a blast lamp or in a muffle furnace at 1100° to 1150°C. to constant weight. Cool in a desiccator, and weigh.

(d) Add sufficient  $\text{H}_2\text{SO}_4$  (1:1) to moisten the  $\text{SiO}_2$ , and then a small amount of  $\text{HF}$ . Evaporate to dryness, ignite at 1000°C., and weigh. The loss in weight represents  $\text{SiO}_2$ .

(e) Calculation.—Calculate the percentage of silicon as follows:

$$\text{Silicon, per cent} = \frac{A \times 0.4672}{B} \times 100$$

where  $A$  = grams of  $\text{SiO}_2$  and

$B$  = grams of sample used.

<sup>21</sup> The solution should preferably contain not more than 2% by volume of  $\text{HCl}$  at the time of the precipitation with  $\text{BaCl}_2$ . Ordinarily, there will be no hydrolysis of iron during the filtration and washing of the undissolved zinc or the precipitation with  $\text{BaCl}_2$ . Should this occur, the solution must be cleared by the addition of  $\text{HCl}$ , having due regard to the final permissible acidity.

<sup>22</sup> This recovery of  $\text{BaSO}_4$  ordinarily represents from 0.001 to 0.003% of sulfur.



2. *Silicomanganese and Manganese-Silicon*.—(a) Transfer 0.5 g. of the sample of silicomanganese (60 to 70% manganese) or 0.25 g. of manganese-silicon (20 to 25% manganese) to an iron crucible. Add 8 g. of dry  $\text{Na}_2\text{O}_2$ , mix, and fuse. Transfer the cold cake to a dry 500-ml. porcelain casserole, cover, and add 80 ml. of  $\text{H}_2\text{SO}_4$  (1:1). When acidifying the solution of the fusion with  $\text{H}_2\text{SO}_4$ , it is necessary to add some  $\text{H}_2\text{SO}_4$  to dissolve the  $\text{MnO}_2$  that may separate. When all action ceases, rinse the crucible well with water, add the rinsings to the casserole, and evaporate to dense white fumes.

(b) Complete the determination as described in Section 1 (b) to (c).

(c) When high accuracy is desired, it is advisable to evaporate the filtrate and again dehydrate, filter, etc., to recover the small amount of  $\text{SiO}_2$  that escaped the first dehydration.

### FERROBORON (E31-60T)

*Scope and Application*.—These methods cover the chemical analysis of ferroboron having chemical compositions within the following limits:

Boron, per cent. ....	10	to	20.0
Silicon, max., per cent. ....	0.1	to	5.0
Carbon, max., per cent. ....	0.1	to	3.0
Aluminum, max., per cent. ....	0.01	to	0.50

### BORON BY THE ION-EXCHANGE METHOD

*Scope*.—This method covers the determination of boron in the range from 10 to 20%.

*Summary of Method*.—The sample is fused with sodium peroxide and the fusion leached with acid under a reflux condenser, transferred to a beaker, diluted, and passed through a column of a strong acid-type ion-exchange resin to remove interfering cations. The effluent is nearly neutralized, refluxed to remove carbon dioxide, and cooled. After adjusting the pH, invert sugar or mannitol is added, and the solution titrated potentiometrically to pH 6.9 with standard sodium hydroxide solution.

*Apparatus*. (a) Florence Flasks.—These should have 250- and 500-ml. capacity (low-boron).

(b) Reflux Condenser.—The condenser should be equipped with an inner tube made of low-boron glass.

(c) Iron Crucible.—Iron, 30-ml. crucibles made from No. 20 gauge (0.038 in.) ingot iron are suitable.

(d) Ion-Exchange Column.—Prepare by substituting for the zinc column in a Jones Reductor (Fig. 25-1) a column of a suitable ion-exchange resin (see (c), p. 776).

The Jones Reductor shall conform to the dimensional requirements shown in Fig. 25-1.

(e) pH Meter.—This should be provided with outside electrodes and stirrer.

*Reagents and Materials*. (a) Boron, Standard Solution (1 ml. = 0.00054 g. B).—Pulverize 5 g. of boric acid ( $\text{H}_3\text{BO}_3$ ) to pass a No. 60 (250- $\mu$ ) sieve and dry in vacuum over anhydrous magnesium perchlorate<sup>23</sup> at room temperature to con-

<sup>23</sup> Anhydron has been found satisfactory for this purpose.

stant weight. Dissolve 3.092 g. of the dry salt in 500 ml. of hot water. Cool to 100m temperature, and dilute to 1000 ml. with cold, recently boiled water. One milliliter of this solution is equivalent to 0.00051 g. of boron.

(b) Ferrous Sulfate ( $\text{FeSO}_4$ ).

(c) Ion-Exchange Resin.<sup>24</sup>—This should have 8% cross linkage, passing a No. 50 (297- $\mu$ ) sieve but retained on a No. 100 (149- $\mu$ ) sieve.

(d) Invert Sugar Solution (1515 g. per liter).—Dissolve 1000 g. of granulated sugar in 650 ml. of previously boiled hot water and add 8 ml. of 1 *N* HCl. Heat at 80° to 90°C. for 2 hr. Adjust to pH 6.9 with NaOH solution just before use.

(e) Mannitol.—Mannitol, neutral, may be used instead of invert sugar in Paragraph (d).

(f) Methyl Orange Indicator (1 g. per liter).

(g) Sodium Hydroxide, Standard Solution (1 ml. = 0.0011 g. B).—Prepare as directed except that the sodium hydroxide (NaOH) shall be dissolved in a polyethylene beaker and stored in a polyethylene bottle. Standardize the solution against 50 ml. of the standard boron solution, since the relation is not stoichiometric. The actual boron equivalent of the NaOH is 1 to 2% above the theoretical.

(h) Sodium Peroxide ( $\text{Na}_2\text{O}_2$ ).

**Procedure.**—(a) Transfer 1 g. of the sample, weighed to the nearest 0.5 mg., to a 30-ml. iron crucible and mix well with 10 g. of  $\text{Na}_2\text{O}_2$ . Put on goggles, and fuse the mixture carefully by first playing the flame of a laboratory burner cautiously on the surface of the mixture until fusion begins, and then revolving the crucible

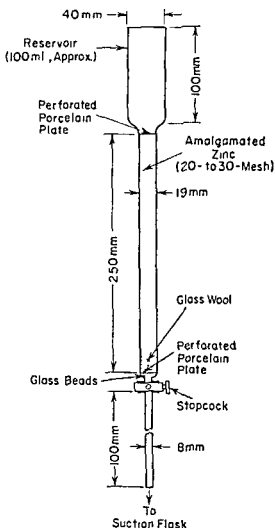


FIG. 25-1. Jones Reductor.

in the outer edge of the flame by gripping with a pair of tongs and rotating vigorously, gradually raising the temperature to about 900°C., until decomposition is complete.

(b) Cover the crucible, cool to 100m temperature, and tap on a solid object to loosen the cake. Transfer the cake to a 250-ml. Florence flask, and connect to the reflux condenser. Mix 30 ml. of HCl with 20 ml. of water, and rinse the crucible with successive portions, adding the rinsings to the flask through the condenser. This should decompose the cake and render the solution just acid. If not, add enough HCl to make the solution just acid to litmus, and boil gently for 5 to 10 min. Cool, disconnect the flask from the condenser, add 1 g. of  $\text{FeSO}_4$ , agitate

<sup>24</sup> Dowex-50 resin has been found suitable for this purpose.

the flask, and blow a current of air on the surface of the solution to expel chlorine. Transfer the solution to a 250-ml. volumetric flask and dilute to the mark. By means of a pipet, transfer 50 ml. of the solution, equivalent to 0.2 g. of the sample, to a 150-ml. beaker, and dilute to 100 ml.

(c) Place a 4-cm. plug of glass wool in the bottom of the ion-exchange column. Fill the tube with resin and wash, first with 100 ml. of HCl (1:2), and then with water to remove the acid. During the washing process adjust the flow rate to approximately 20 ml. per min. Pass the 100-ml. sample through the resin column, and wash the column with 200 ml. of water in successively small portions. Regenerate the resin before reuse by washing with HCl (1:2) until the iron is removed, and finally with water to remove the acid.

(d) Transfer the eluate to a 500-ml. flask of low-boron glass, add 5 drops of methyl orange indicator, and nearly neutralize by addition of NaOH pellets. Boil the solution under a reflux condenser for 5 min. to remove any carbon dioxide (CO<sub>2</sub>) present, cool to room temperature, and transfer to a 600-ml. beaker.

(e) Using a pH meter, adjust the solution to pH 6.9 by addition of 0.1 *N* NaOH solution from a buret. Add sufficient invert sugar solution or mannitol to make the resulting concentration 0.6 *M* (13 ml. invert sugar solution or 11 g. of mannitol per 100 ml. of solution). Titrate immediately to pH 6.9 with 0.1 *N* NaOH solution.

(f) Blank.—Make a blank determination following the same procedure and using the same quantities of all reagents.

Calculation.—Calculate the percentage of boron as follows:

$$\text{Boron, per cent} = \frac{(A - B)C}{D} \times 100$$

where *A* = milliliters of NaOH solution required for titration of the sample,

*B* = milliliters of NaOH solution required for titration of the blank,

*C* = boron equivalent of the NaOH solution, and

*D* = grams of sample used.

## ALUMINUM BY THE AURINTRICARBOXYLIC ACID (ALUMINON) (PHOTOMETRIC) METHOD (E31-60T)

*Scope.*—This method covers the determination of aluminum in the range from 0.01 to 0.50%.

*Summary of Method.*—After fusion of the sample with sodium peroxide and leaching with water, an aliquot of the supernatant liquid is acidified, and the aluminum concentrated by precipitation with ammonium hydroxide. Iron is separated with cupferron, the excess cupferron in the filtrate destroyed with nitric and perchloric acids, and aluminum determined photometrically with aluminon reagent.

*Concentration Range.*—The recommended concentration range is from 0.02 to 0.10 mg. of aluminum in a 100-ml. volume using a cell depth of 2 cm. (NOTE 7).

*Note 7.*—This method has been written for a cell having a 2-cm. light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amount of sample and reagents used.

*Stability of Color.*—The color has an appreciable temperature coefficient, and all measurements should be made within  $\pm 1^\circ\text{C.}$  of the selected operating temperature.

**Interferences.**—Provision for removal of interfering elements normally present in ferroboron has been made.

**Precautions.**—See the paragraph on perchloric acid under "Water, Reagents, and Glassware," in the section "Standard Methods for Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron, and Wrought Iron," Chapter 21, relative to use of perchloric acid.

**Apparatus.** (a) Volumetric Flasks.—Flasks shall be of borosilicate glass, glass-stoppered, 100- and 200-ml. capacity.

(b) Iron Crucible, 50-ml.

**Reagents.** (a) Aluminum, Standard Solution (1 ml. = 1.00 mg. Al).—Transfer 1.00 g. of high-purity aluminum to a 1-liter volumetric flask. Add 100 ml. of HCl (1:1), and heat gently until dissolution is complete. Cool to room temperature, dilute to the mark, and mix well.

(b) Aluminum, Standard Solution (1 ml. = 0.0100 mg. Al).—Transfer 10.0 ml. of aluminum solution (1 ml. = 1.00 mg. Al) to a 1-liter volumetric flask, add 20 ml. of HCl (1:1), dilute to the mark with water, and mix well.

(c) Aluminon-Buffer Solution.—Dissolve 125 g. of ammonium acetate ( $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ) in 250 ml. of water and 20 ml. of glacial acetic acid, and filter through a dry filter. Dissolve 0.250 g. of ammonium aurintricarboxylate (aluminon) in 50 ml. of water, and add to the ammonium acetate-acetic acid solution.

Dissolve 0.50 g. of benzoic acid in 20 ml. of methanol and add slowly with good stirring to the acetate-aluminon solution. Dilute the combined solutions to 500 ml. with water. Add 250 ml. of glycerol with good stirring, and transfer the solution to a dark-colored, glass-stoppered bottle. Store in a dark place, and let stand for 72 hr. before using.

(d) Ammonium Chloride Wash Solution (20 g. per liter).—Dissolve 20 g. of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) in 200 ml. of water, and dilute to 1 liter.

(e) Bromocresol Purple Indicator (0.1 g. per liter).—Dissolve 0.1 g. of bromocresol purple in 1.85 ml. of 0.1000 *N* NaOH solution and dilute with water to 250 ml.

(f) Cupferron Solution (60 g. per liter).—Dissolve 6 g. of cupferron in 80 ml. of cold water, dilute to 100 ml., and filter. Prepare fresh as needed.

(g) Cupferron Wash Solution.—Add 20 ml. of cupferron solution to 980 ml. of  $\text{H}_2\text{SO}_4$  (1:9).

(h) *p*-Nitrophenol Indicator (0.20 g. per liter).—Dissolve 0.020 g. of *p*-nitrophenol in 100 ml. of water.

(i) Sodium Peroxide ( $\text{Na}_2\text{O}_2$ ).

(j) Thioglycolic Acid Solution (10 ml. per liter).—Dilute 1 ml. of thioglycolic acid to 100 ml. with water. This solution is not stable and should be prepared as needed.

**Preparation of Calibration Curve.** (a) Calibration Solutions.—(1) By means of a buret, transfer 2.0-, 4.0-, 6.0-, 8.0-, and 10.0-ml. aliquots of the standard aluminum solution (1 ml. = 0.0100 mg. Al) to five 100-ml. volumetric flasks, and carry a sixth 100-ml. volumetric flask along as a blank. Add 2 ml. of  $\text{HClO}_4$  to each flask and dilute to 20 ml. with water.

(2) Add 3 drops of the *p*-nitrophenol indicator. Neutralize to a yellow color with  $\text{NH}_4\text{OH}$ . Immediately add HCl (1:1) dropwise until the solution is colorless, and then add 1 drop in excess. Add 0.2 ml. of thioglycolic acid solution and 15 ml. of the aluminon-buffer solution. Since the latter solution is viscous, allow the pipet to drain for a few minutes. Place the 100-ml. volumetric flask in a 400-

ml. beaker containing boiling water. Heat for exactly 4 min. while maintaining the water in the beaker at the boiling point. Remove from the 400-ml. beaker, and cool in the air for 1 min. Cool in running water for 4 min. Dilute to the mark and mix.

(b) *Photometry*.—Transfer water to a 2-cm. photometer cell, and adjust the photometer to the initial setting, using a light band centered at approximately 540 m $\mu$ . Transfer a suitable portion of the test solution, adjusted to 25°  $\pm$  1°C., to a matched 2-cm. photometer cell, and take the photometric readings of the calibration solutions.

(c) *Calibration Curve*.—Plot the photometric readings of the calibration solutions against milligrams of aluminum per 100 ml. of solution, corrected for the blank if necessary.

*Procedure*.—(a) Transfer 2 g., weighed to the nearest 1 mg., of the sample passing a No. 100 (149- $\mu$ ) sieve to a 50-ml. iron crucible containing 18 g. of Na<sub>2</sub>O<sub>2</sub>, mix well, and cover with 2 g. of Na<sub>2</sub>O<sub>2</sub>. Put on goggles and cautiously heat over the flame of a burner until the melt begins to fuse, and then increase the temperature and continue heating for 4 to 5 min., rotating the crucible until the sample is completely decomposed. Cover the crucible, cool, tap on a hard surface to loosen the melt, and transfer to a weighed, 1200-ml. stainless steel beaker. Cautiously add 300 ml. of water. When the reaction has ceased, wash the crucible with hot water and add the washings to the beaker. Add 200 ml. of water, 1 to 2 g. of Na<sub>2</sub>O<sub>2</sub>, and boil for 5 min. to oxidize any chromium present. Cool, and add water to make 1000 g. of solution. Mix well, allow to settle, and decant 750 g. of the solution into another stainless steel beaker. Nearly neutralize the solution with H<sub>2</sub>SO<sub>4</sub> (1:1) and transfer to a 1500-ml. glass beaker containing 10 ml. of H<sub>2</sub>SO<sub>4</sub> (1:1). The solution should be acid to litmus; if not, add sufficient H<sub>2</sub>SO<sub>4</sub> (1:1) until an acid reaction is obtained.

(b) Add 4 to 5 drops of bromocresol purple indicator and NH<sub>4</sub>OH (1:1) until the color of the solution just changes to purple. Boil for 1 min., let settle, filter using a 9-cm. medium paper containing a little paper pulp, and wash 12 to 15 times with hot NH<sub>4</sub>Cl wash solution. Transfer the paper and precipitate to a 400-ml. beaker. Add 30 ml. of HNO<sub>3</sub> to the 1500-ml. beaker in which the precipitation was made, heat to dissolve any precipitate adhering to the sides of the beaker, and transfer the solution to the 400-ml. beaker containing the paper and precipitate. Add 15 ml. of HClO<sub>4</sub> and evaporate to copious white fumes (Caution) to destroy all organic matter. Cool, add 20 ml. of HCl, and again evaporate to copious white fumes to volatilize any chromium present.

(c) Cool, add 100 ml. of HCl (15:85), heat to boiling, and cool to 15° to 20°C. Add a slight excess of cold cupferron solution, stir well, let settle, filter through an 11-cm. medium paper into a 400-ml. beaker, and wash 12 to 15 times with cold cupferron wash solution. Discard the precipitate.

(d) To the filtrate add 30 ml. of HNO<sub>3</sub> and 10 ml. of HClO<sub>4</sub>, and evaporate to copious white fumes (Caution). Cool, and wash down the cover and sides of the beaker with water. Again evaporate to copious white fumes and continue fuming until the volume is reduced to 2 ml. Cool, add 50 ml. of water, heat to boiling, and filter into a volumetric flask through a 9-cm. medium paper containing a little paper pulp. The size of the flask and subsequent dilution of the filtrate are based on the following ranges in aluminum content of the alloy:

<i>Aluminum, per cent</i>	<i>Final Solution Volume, ml.</i>
0.01 to 0.05 . . . . .	200
0.05 to 0.25 . . . . .	500
0.20 to 0.50 . . . . .	1000

Wash the paper 12 to 15 times with hot water and discard. Cool the solution to room temperature, dilute to the mark with water, and mix well.

(e) Transfer an aliquot containing from 0.01 to 0.10 mg. of aluminum to a 100-ml. volumetric flask, and dilute to 20 ml. with water. Proceed as directed under calibration curve preparation, Paragraphs (a)(2) and (b) (NOTE 8). Carry a blank determination through all the steps of the procedure.

NOTE 8—If more than 10 drops of  $\text{NH}_4\text{OH}$  are required to neutralize the solution, discard, pipet another aliquot, evaporate to fumes of  $\text{HClO}_4$ , and fume until the volume is reduced to incipient dryness. Too large an excess of acid causes precipitation of the aluminum lake when neutralized with  $\text{NH}_4\text{OH}$ .

**Calculation.**—By means of the calibration curve, convert the photometric readings of the sample and blank solution to milligrams of aluminum. Calculate the percentage of aluminum as follows:

$$\text{Aluminum, per cent} = \frac{A - B}{C \times 10}$$

where  $A$  = milligrams of aluminum in the sample aliquot used,

$B$  = milligrams of aluminum in the blank, and

$C$  = grams of sample in the aliquot used.

### SILICON BY THE SULFURIC ACID METHOD (E31-60T)

**Scope.**—This method is recommended for the determination of silicon in the range from 0.1 to 5.0%.

**Summary of Method.**—The sample is fused with sodium peroxide in an iron crucible, the melt transferred to a casserole, where it is acidified with sulfuric acid, and evaporated to dense white fumes. After dilution of the acid, the dehydrated silicon is filtered, ignited in platinum, weighed, and volatilized with hydrofluoric and sulfuric acids. The platinum crucible is again weighed and the silicon determined by difference.

**Apparatus.** Iron Crucible, 30-ml.

**Reagents.** Sodium Peroxide ( $\text{Na}_2\text{O}_2$ ).

**Procedure.**—(a) Mix 0.5 g. of the sample with 10 g. of  $\text{Na}_2\text{O}_2$  in a 30-ml. iron crucible. Put on goggles, and fuse the mix carefully by revolving the crucible in the outer edge of the flame of a laboratory burner at a temperature of  $700^\circ$  to  $800^\circ\text{C}$ . As the mixture begins to fuse, rotate the crucible vigorously to stir up any unattacked particles adhering to the bottom and sides; increase the temperature and continue heating for 3 to 4 min. longer. Cover with a lid and allow to cool almost to room temperature; then tap on a solid object to loosen the melt.

(b) Transfer the cold cake to a dry, 500-ml. porcelain casserole (having a good glaze), add 80 ml. of  $\text{H}_2\text{SO}_4$  (1:1), rinse the crucible with hot water, adding the washings to the casserole, and evaporate to dense white fumes.

**Standardization against Potassium Dichromate.**—To prepare pure  $K_2Cr_2O_7$  recrystallize, at least twice, the purest grade of the salt obtainable, dry the crystals at  $150^\circ C.$ , and fuse in platinum at  $415^\circ C.$  Grind to approximately 80-mesh and preserve in a glass-stoppered bottle. Transfer 1.0000 g. of the pure  $K_2Cr_2O_7$ , which contains approximately the same amount of chromium as a 0.5-g. sample of 70% ferrochromium, to an 800-ml. beaker. Dissolve in cold water, acidify with 40 ml. of  $H_2SO_4$  (1:3), and dilute with cold water to 500 ml. Add a slight excess of the ferrous ammonium sulfate solution (approximately 190 ml.), and titrate the excess ferrous ammonium sulfate with 0.1 N  $KMnO_4$  to the first faint permanent darkening of the clear green color.

**EXAMPLE.**—The calculations involved in determining the normality of the ferrous ammonium sulfate solution are illustrated as follows:

In a standardization, 190.0 ml. of the ferrous ammonium sulfate solution was used and 5.06 ml. of 0.1 N  $KMnO_4$  was required to titrate the excess.

1 ml. of 0.1 N  $K_2Cr_2O_7$  contains 0.001903 g. of  $K_2Cr_2O_7$

1 g. of  $K_2Cr_2O_7$  = 203.94 ml. of 0.1 N  $K_2Cr_2O_7$

then:

$203.94 + 5.06 = 209.0$  ml. of equivalent 0.1 N solution reduced by the ferrous ammonium sulfate solution

$$\text{Normality} = \frac{209.0}{190} \times 0.1 = 0.11$$

**Standardization against Sodium Oxalate.**—In standardizing against sodium oxalate through  $KMnO_4$ , it is necessary to add the ferrous ammonium sulfate solution by means of a calibrated pipet or buret instead of an automatic pipet. Transfer 100 ml. of the ferrous ammonium sulfate solution to a 600-ml. beaker, dilute to 300 ml. with cold  $H_2SO_4$  (5:95), add 2 ml. of  $H_3PO_4$  (85%), and titrate immediately with 0.1 N  $KMnO_4$  to a faint permanent pink color. Correct the volume of  $KMnO_4$  by the volume required to give the same tint in the same volume of water and acids. When this method is used, it is necessary in the actual analysis to determine a blank to counteract the influence of the green color of the chromium sulfate upon the  $KMnO_4$  end point. This blank may be determined in the solution used in the analysis, as described in Paragraph (d) of the following section.

(d) Ammonium Persulfate Solution (150 g. per liter).

(e) Standard Potassium Permanganate Solution (0.1 N).

**Procedure.**—(a) Transfer 0.5 g. of the sample to a 30-ml. iron crucible and add 8 g. of dry  $Na_2O_2$ . Thoroughly mix the contents of the crucible with a small rod, being careful to clean the rod, which may be done conveniently by scraping with another rod. Cover the mixture with an additional 1 to 2 g. of  $Na_2O_2$ . Cover the crucible with a nickel cover and carefully fuse the contents, preferably in an electric muffle heated to  $600^\circ$  to  $700^\circ C.$  Fusion for 5 min. at a low red heat after the mix has melted will result in complete decomposition. When the charge has melted, the crucible should be given a slight rotary motion to stir up any unattached particles.

(b) Place the cooled crucible and cover in a 600-ml. covered beaker, and dissolve the contents in 150 ml. of water. When the melt had dissolved, remove the crucible, cover, and rinse. Add to the solution 60 ml. of  $H_2SO_4$  (1:1) and 5 ml. of  $HNO_3$ , and boil for several minutes until all iron scale from the crucible is dissolved. Add 5 to 10 ml. of  $AgNO_3$  (5 g. per liter), 2 to 4 drops of  $KMnO_4$  (25 g. per liter), and 3 to 5 g. of  $(NH_4)_2S_2O_8$ , and boil for 10 min. Add from 3 to 5 ml.

## TOTAL CARBON BY THE DIRECT-COMBUSTION METHOD

*Procedure.*—Determine carbon by the direct-combustion method (p. 765), with the following modification: use 0.25 to 0.50 g. of the sample for high-carbon ferrochromium, and 1.5 to 2 g. of the sample for low-carbon ferrochromium.

## SILICON BY THE SULFURIC ACID METHOD

*Procedure. 1. Low-Carbon Ferrochromium and Chromium Metal.*—(a) Transfer 1 to 2 g. of the sample to a 250-ml. porcelain casserole, add 10 ml. of  $H_2SO_4$  (1:1), and warm the covered casserole gently until the reaction is complete.

(b) Evaporate the solution to white fumes. If chromium sulfate solutions are fumed at too high temperatures or for any great length of time or with too little free acid present, considerable difficulty will occur in dissolving the salts. The fuming should, therefore, be made at a temperature not much higher than that required for evolving the acid. Allow the casserole and contents to cool somewhat (if permitted to become entirely cold, difficulty may be experienced in getting chromium salts to dissolve), add 150 ml. of warm water while stirring to prevent the residue from caking on the bottom, and boil the solution gently for several minutes to dissolve all salts. Filter, and wash the paper several times with hot HCl (5:95) and then with warm water.

(c) Transfer the filter paper and contents to a platinum crucible, char the paper without flaming, carefully ignite to remove carbon, and then heat the covered crucible over a blast lamp or in a muffle furnace at  $1100^\circ$  to  $1150^\circ C.$  to constant weight. Cool in a desiccator and weigh.

(d) Add sufficient  $H_2SO_4$  (1:1) to moisten the residue and then a small amount of HF. Evaporate to dryness, ignite at  $1000^\circ C.$ , and weigh. The loss in weight represents  $SiO_2$ .

(e) Calculation.—Calculate the percentage of silicon as follows:

$$\text{Silicon, per cent} = \frac{A \times 0.4672}{B} \times 100$$

where  $A$  = grams of  $SiO_2$ , and

$B$  = grams of sample used.

*2. Ferrochromium Containing Over 1% Carbon.*—(a) Transfer 1 g. of the sample to a 30-ml. iron crucible, and add 8 g. of dry  $Na_2O_2$ . Thoroughly mix the contents of the crucible with a small rod, being careful to clean the rod which may be done conveniently by scraping with another rod. Cover the mixture with 1 to 2 g. of  $Na_2O_2$ . Cover the crucible and carefully fuse the contents, preferably in an electric muffle heated to  $600^\circ$  to  $700^\circ C.$  Fusion for 5 min. at a low red heat after the mix has melted will result in complete decomposition. When the charge has melted, the crucible should be given a slight rotary motion to stir up any unattacked particles.

(b) When the fusion has solidified, tap the covered crucible, while still warm, on an iron plate to loosen its contents in a solid cake. Transfer the melt to a dry 250-ml. porcelain casserole, cover, and immediately add 80 ml. of  $H_2SO_4$  (1:1). Rinse the crucible with warm water and add the rinsings to the solution in the casserole. When action is complete, rinse, and remove the cover.

(c) Complete the determination as described in Section 1 (b) to (e).



18°C. or less, oxidize the excess of ferrous iron with 8 ml. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (150 g. per liter), and stir the solution vigorously for exactly 60 sec.

(c) Titrate the solution (at 18° to 20°C.) with 0.1 *N*  $\text{KMnO}_4$ , while stirring constantly, until a faint pink color appears that persists for 30 sec.

(d) Blank.—Make a blank determination by dissolving 0.4 g. of ingot iron in 60 ml. of  $\text{H}_2\text{SO}_4$  (1:3) and 5 ml. of  $\text{HNO}_3$ , and following the same procedure as with the sample. If the alloy contains an appreciable amount of chromium, dissolve in the acids with the ingot iron a weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  equivalent to the amount of chromium in the sample.

(e) Calculation.—Calculate the percentage of vanadium as follows:

$$\text{Vanadium per cent} = \frac{(A - B)C \times 0.05095}{D} \times 100$$

where *A* = milliliters of  $\text{KMnO}_4$  solution required for titration of the sample,

*B* = milliliters of  $\text{KMnO}_4$  solution required for titration of the blank,

*C* = normality of the  $\text{KMnO}_4$  solution, and

*D* = grams of sample used.

### TOTAL CARBON BY THE DIRECT-COMBUSTION METHOD

*Procedure.*—Determine carbon by the direct-combustion method in accordance with the procedure for ferrosilicon (p. 765), with the following modification.

A furnace temperature of 1150° to 1200°C. will suffice for ferrovanadium, and complete combustion, except in very high-silicon material, can be secured without the addition of an accelerator.

### PHOSPHORUS BY THE ALKALIMETRIC METHOD

*Reagents.* (a) Perchloric Acid (70%).

(b) Ammonium Molybdate Solution (65 g. per liter).—Transfer 65 g. of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  to a 1-liter beaker and add 40 ml. of  $\text{NH}_4\text{OH}$ . Add 600 ml. of water and 100 g. of  $(\text{NH}_4)_2\text{SO}_4$ ,<sup>28</sup> stir, and heat gently until in solution. Filter, without washing, dilute to 1 liter with water, and mix well.

(c) Hydrobromic Acid (48%).

(d) Potassium Permanganate Solution (25 g. per liter).

(e) Ammonium Molybdate Solution (Acidic).

(f) For descriptions of other reagents required, see reagents for determining phosphorus in ferrosilicon.

*Procedure.*—(a) Transfer 2 g. of the sample to a 200-ml. platinum dish, cover, and cautiously dissolve in 50 ml. of  $\text{HNO}_3$  (1:2). When the reaction has subsided, wash down the cover and dish, and remove the cover. Add 3 to 5 ml. of  $\text{HF}$ , and digest for about 5 min.

(b) Add 25 ml. of  $\text{HClO}_4$  (70%), place on a triangle or sand bath, and evaporate to fumes of  $\text{HClO}_4$ . This evaporation must be conducted with care, as most of the vanadium separates as  $\text{V}_2\text{O}_5$ , and the mixture has a tendency to bump. Continue the gentle fuming for 5 to 10 min. to remove most of the  $\text{HNO}_3$  and  $\text{HF}$ , and cool.<sup>29</sup>

<sup>28</sup> In this ammonium molybdate solution  $(\text{NH}_4)_2\text{SO}_4$  replaces the usual  $\text{NH}_4\text{NO}_3$ .

<sup>29</sup> Care should be taken that not more than 5 ml. of  $\text{HClO}_4$  is expelled; otherwise, add an additional 5 to 10 ml. of  $\text{HClO}_4$  before proceeding. Too great a loss of  $\text{HClO}_4$  may result in little if any of the phosphorus being precipitated later upon the addition of ammonium molybdate.

warm to 50° to 60°C., and add 25 ml. of  $\text{BaCl}_2$  (100 g. per liter). Stir well and let stand at room temperature for 24 to 40 hr.

(c) Filter, with as little transfer of the precipitate as possible, through a close-texture paper. Wash the paper 2 or 3 times with cold  $\text{HCl}$  (1:99) and 7 times with warm water.

(d) Ignite the paper and contents in a platinum crucible. Dissolve the ignited residue with 5 ml. of  $\text{HCl}$ , and transfer the solution to the original beaker containing most of the precipitate of  $\text{BaSO}_4$  (Paragraph (c)). Digest the combined portions of  $\text{BaSO}_4$  so as to dissolve any barium vanadate. Adjust the volume of the solution to 150 ml., and the acidity to 2% by volume of  $\text{HCl}$ . Add 8 ml. of  $\text{BaCl}_2$  (100 g. per liter), and allow to stand for 24 hr. Filter on a close-texture paper and wash 3 times with cold  $\text{HCl}$  (1:99) and 10 times with warm water.<sup>31</sup>

(e) Ignite in platinum, cool in a desiccator, and weigh as  $\text{BaSO}_4$ .

(f) Blank.—Make a blank determination, following the same procedure and using the same amounts of all reagents.

(g) Calculation.—Calculate the percentage of sulfur as follows:

$$\text{Sulfur, per cent} = \frac{(A - B) \times 0.1374}{C} \times 100$$

where  $A$  = grams of  $\text{BaSO}_4$ ,

$B$  = correction for blank, in grams and

$C$  = grams of sample used.

### SILICON BY THE NITRIC-SULFURIC ACID METHOD

**Reagents.** Nitric-Sulfuric Acid Mixture.—Slowly stir 160 ml. of  $\text{H}_2\text{SO}_4$  into 660 ml. of water, and add 180 ml. of  $\text{HNO}_3$ .

**Procedure.** 1. *Low- or Medium-Silicon Ferrovanadium.*—(a) Dissolve 1 to 2 g. of the sample in 40 ml. of the  $\text{HNO}_3$ - $\text{H}_2\text{SO}_4$  mixture in a 250-ml. porcelain or platinum dish, and evaporate the solution to dense white fumes.

(b) Cool the solution, add 125 ml. of water, and heat for a few minutes, while stirring frequently, until all salts are dissolved. Immediately filter on a 9-cm. paper. Wash the precipitate with hot  $\text{HCl}$  (5:95) and cold water alternately to complete the removal of iron salts, and finally wash with hot water until free of acid.

(c) Transfer the filter paper and contents to a platinum crucible, char the paper without flaming, and finally ignite the covered crucible over a blast lamp or in a muffle furnace at 1100° to 1150°C. to constant weight. Cool in a desiccator and weigh.

(d) Add sufficient  $\text{H}_2\text{SO}_4$  (1:1) to moisten the  $\text{SiO}_2$ , and then a small amount of  $\text{HF}$ . Evaporate to dryness, ignite at 1000°C., and weigh. The loss in weight represents  $\text{SiO}_2$ .

(e) Calculation.—Calculate the percentage of silicon as follows:

tion to dryness, fuse with  $\text{Na}_2\text{CO}_3$ , and add the water extract of the melt to the main solution.

<sup>31</sup> If desired, the washings may be kept separate and examined for  $\text{BaSO}_4$  as follows: evaporate the washings to dryness; dissolve the slight residue in 50 ml. of hot  $\text{HCl}$  (2:98); add 2 ml. of  $\text{BaCl}_2$  (100 g. per l.); and digest at 70° to 80°C. for 2 hr., avoiding any undue evaporation; filter on a small close-texture paper; wash 3 times with cold  $\text{HCl}$  (1:99), and 10 times with warm water. The recovery of  $\text{BaSO}_4$  that is ordinarily obtained represents approximately 0.001 to 0.002% of sulfur.

$$\text{Silicon, per cent} = \frac{A \times 0.4672}{B} \times 100$$

where  $A$  = grams of  $\text{SiO}_2$ , and  
 $B$  = grams of sample used.

2. *High-Silicon Ferrovandium*.—(a) Ferrovandium containing 4% or more of silicon is not completely soluble in  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . In this case, thoroughly mix 1 g. of the sample with 8 g. of dry  $\text{Na}_2\text{O}_2$  and fuse in a 30-ml. iron crucible. After the contents of the crucible have melted, continue heating for 5 min. longer at a dull red heat to ensure complete decomposition of the sample. Allow the fusion to solidify, but before it has entirely cooled, tap the covered crucible on an iron plate, which will loosen the contents in a solid cake. Transfer the melt to a dry 250-ml. porcelain casserole, and add immediately, with caution, 80 ml. of  $\text{H}_2\text{SO}_4$  (1:1). Rinse the crucible with warm water, and cautiously add the solution to the covered casserole. Remove the cover and rinse it with water and then evaporate to dense white fumes.

(b) Complete the determination in accordance with Paragraphs (b) to (c) above.

### ALUMINUM BY THE CUPFERRON-PHOSPHATE METHOD

*Reagents.* (a) Potassium Permanganate Solution (25 g. per liter).

(b) Cupferron Solution (60 g. per liter).—Dissolve 6 g. of cupferron in 80 ml. of cold water, dilute to 100 ml., and filter. Prepare fresh as needed.

(c) Cupferron Wash Solution.—Dilute 20 ml. of cupferron solution (60 g. per liter) to 1 liter with cold  $\text{H}_2\text{SO}_4$  (1:9).

(d) Perchloric Acid (70%).

(e) Bromcresol Purple Indicator Solution (0.1 g. per liter).—Dissolve 0.1 g. of bromcresol purple in 1.85 ml. of 0.1000  $N$   $\text{NaOH}$  solution and dilute with water to 250 ml.

(f) Ammonium Acetate Solution (200 g. per liter).

(g) Methyl Red Indicator Solution (0.1 g. per liter).—Dissolve 0.1 g. of methyl red in 3.72 ml. of 0.1000  $N$   $\text{NaOH}$  solution and dilute to 250 ml. with water. Filter if necessary.

*Procedure.*—(a) Decompose 1 g. of the sample with 60 ml. of  $\text{H}_2\text{SO}_4$  (1:2) and 10 ml. of  $\text{HNO}_3$ . If an insoluble residue remains, add 2 to 3 ml. of  $\text{HF}$ , after transferring to platinum. Heat to dense white fumes, cool somewhat, add water, and heat until salts are dissolved. Add  $\text{KMnO}_4$  (25 g. per liter) to the hot solution, until a pink color persists. Dilute to 100 ml. and cool to 5° to 10°C. in ice water. Add a large amount of ashless paper pulp, and precipitate the iron and vanadium by adding cupferron (60 g. per liter) until an excess of reagent is shown by the appearance of a white curdy precipitate instead of the brown one first formed. Stir vigorously for 2 to 3 min., and filter on 2 superimposed 11-cm., medium-texture filter papers (containing some ashless paper pulp) supported on a Büchner funnel, using moderate suction. Wash thoroughly with cupferron wash solution.

(b) In the analysis of alloys of high aluminum content, or for very accurate work, return the cupferron precipitate to the original beaker and add 10 ml. of  $\text{H}_2\text{SO}_4$ , 50 ml. of  $\text{HNO}_3$ , and 5 ml. of  $\text{HClO}_4$  (70%). Evaporate slowly to dense white fumes to completely destroy all organic matter. Add more  $\text{HNO}_3$ , if necessary, and repeat the evaporation to dense white fumes. Cool, add 100 ml. of water, and digest until all salts are in solution. Cool to 5° to 10°C., add an excess of  $\text{KMnO}_4$ .

(25 g. per liter), and repeat the precipitation with cupferron, the filtration, and the washing.

(c) To the filtrate, or filtrates and washings, add 75 ml. of  $\text{HNO}_3$  and 10 ml. of  $\text{HClO}_4$  (70%). Evaporate until fumes of  $\text{HClO}_4$  appear or until all organic matter is destroyed. The  $\text{HNO}_3$  must always be added before evaporation to fumes of  $\text{HClO}_4$ , as specified. Dilute the cold solution to 100 ml., add 10 g. of  $\text{NH}_4\text{Cl}$  and a few drops of bromocresol purple indicator, and add  $\text{NH}_4\text{OH}$  (1:1) until the solution just turns purple. Boil the solution for 1 min. Allow the precipitate to settle, filter, and wash with warm  $\text{NH}_4\text{Cl}$  (20 g. per liter).

(d) Dissolve the precipitate in 50 ml. of hot  $\text{HCl}$  (1:3) and wash the paper well with hot water. Repeat the precipitation with  $\text{NH}_4\text{OH}$  (1:1) and filter as described in Paragraph (c). Dissolve the precipitate off the paper with 50 ml. of hot  $\text{HCl}$  (1:3), and wash the filter with hot water.

(e) To the filtrate add 0.5 g. of  $(\text{NH}_4)_2\text{HPO}_4$ , a little ashless paper pulp and 2 drops of methyl red indicator, and make just ammoniacal. Restore the pink color by adding  $\text{HCl}$  (1:19) drop by drop. Heat the solution to boiling, and add 20 ml. of ammonium acetate (200 g. per liter). Continue the boiling for 5 min., let settle (1 to 2 hr. if the amount of aluminum is very small), and filter through a 9-cm. paper. Wash with hot  $\text{NH}_4\text{NO}_3$  (50 g. per liter) until 5 ml. of the washings no longer give a test for chlorides with an acidified solution of  $\text{AgNO}_3$ .

(f) Ignite in platinum or porcelain under good oxidizing conditions until carbon is gone. Cover, and heat at about  $1000^\circ\text{C}$ . to constant weight. Weigh as  $\text{AlPO}_4$ .

(g) Blank.—Make a blank determination, following the same procedure and using the same amounts of all reagents.

(h) Calculation.—Calculate the percentage of aluminum as follows:

$$\text{Aluminum, per cent} = \frac{(A - B) \times 0.221}{C} \times 100$$

where  $A$  = grams of  $\text{AlPO}_4$ ,

$B$  = correction for blank, in grams, and

$C$  = grams of sample used.

## FERROTUNGSTEN AND TUNGSTEN METAL

### TUNGSTEN BY THE ACID DIGESTION-CINCHONINE METHOD

**Reagents.** (a) Cinchonine Solution (125 g. per liter).—Dissolve 125 g. of cinchonine in 1 liter of  $\text{HCl}$  (1:1), and filter.

(b) Alpha-Benzoinoxime, Acetone Solution (50 g. per liter).—Dissolve 5 g. of alpha-benzoinoxime in 95 ml. of acetone and 5 ml. of cold water. Filter if necessary. Keep in a dark-colored bottle in a cool place, and do not use when more than 5 days old.

(c) Cinchonine-Benzoinoxime Wash Solution.—Dilute a mixture of 30 ml. of cinchonine solution (Paragraph (a)) and 5 ml. of alpha-benzoinoxime solution (Paragraph (b)) to 1 liter with water.

**Procedure.**—(a) Transfer 1 g. of the sample to a 60-ml. covered platinum crucible, or preferably a large dish, add 5 ml. of  $\text{HF}$ , and then add  $\text{HNO}_3$  drop by drop, while heating, until the sample is dissolved. Remove the cover and rinse it with

water. Add 15 ml. of  $\text{H}_2\text{SO}_4$  (1:1), and heat cautiously on a sand bath to dense white fumes.

(b) Allow to cool, and transfer the residue to a 600-ml. beaker with water; finally wipe the dish with a piece of ashless filter paper and add the paper to the solution. Rinse the crucible or dish with a little warm  $\text{NH}_4\text{OH}$  (1:1), some water, and then a few milliliters of hot  $\text{HCl}$  (1:1). Repeat the treatment with  $\text{NH}_4\text{OH}$  (1:1), water and  $\text{HCl}$  (1:1), and add the rinsings to the 600-ml. beaker. Dilute the contents of the beaker to about 150 ml. with water, add 10 ml. of  $\text{HCl}$ , and boil for 5 min. Remove from the source of heat and dilute to 450 ml. with water. Add 10 ml. of cinchonine solution and some ashless paper pulp, and, while stirring occasionally, digest the solution at  $10^\circ$  to  $15^\circ\text{C}$ . for 30 to 45 min., or preferably overnight. Add 5 ml. of the acetone solution of alpha-benzoinoxime (30 g. per liter), stir vigorously for several minutes, and filter on an 11-cm. paper containing a little ashless paper pulp. Wash thoroughly with cold cinchonine-benzoinoxime wash solution, and finally several times with cold  $\text{HCl}$  (1:99).

(c) Gently ignite the paper and residue in a weighed platinum crucible until the carbon is consumed. Add a few drops of  $\text{HNO}_3$ , and dry on a water or sand bath. Ignite the crucible and  $\text{WO}_3$  for 30 min. at about  $750^\circ\text{C}$ . (to constant weight), cool, and weigh. Ignitions should be made at about  $750^\circ\text{C}$ . in an electric muffle furnace. As  $\text{WO}_3$  is slowly but steadily volatilized at temperatures much above  $750^\circ\text{C}$ ., serious error may result if this temperature is not strictly adhered to as a maximum.

(d) Add about 5 g. of  $\text{Na}_2\text{CO}_3$  to the residue and mix thoroughly. Cover with an additional 1 or 2 g. of  $\text{Na}_2\text{CO}_3$  and fuse, running the fusion around the sides of the crucible or dish to remove all  $\text{WO}_3$ . Dissolve the fusion in hot water, add a little alcohol, heat, and filter. Thoroughly wash the crucible and residue with hot water, and reserve the filtrate.

(e) Place the residue and paper in the crucible and ignite; add a little  $\text{Na}_2\text{CO}_3$  and fuse again. Dissolve the fusion in water, add a little alcohol, and filter and wash thoroughly with hot water to remove the last traces of  $\text{Na}_2\text{CO}_3$ . Combine the filtrate with the filtrate obtained as described in Paragraph (d) and reserve the combined filtrates.<sup>32</sup>

(f) Transfer the residue and paper to a weighed platinum crucible, and ignite. Add 1 or 2 drops of  $\text{H}_2\text{SO}_4$  and 0.5 ml. of  $\text{HF}$ , evaporate to dryness, and ignite again. Cool and weigh.

(g) Determine the amount of insoluble residue in the same weight of  $\text{Na}_2\text{CO}_3$  as was used with the sample (Paragraphs (d) and (e)), following the same procedure.

(h) Calculation.—Calculate the percentage of tungsten as follows:<sup>33</sup>

<sup>32</sup> If the alloy contains molybdenum, the weighed tungstic oxide may contain a few hundredths of a per cent of molybdenum as  $\text{MoO}_3$ . If extreme accuracy is desired, the oxide should be tested photometrically. If the molybdenum content of the alloy is unknown, the  $\text{Na}_2\text{CO}_3$  extract of the impure  $\text{WO}_3$  (see Paragraph (e) above) can be treated with tartaric acid and  $\text{H}_2\text{S}$ , and acidified with  $\text{H}_2\text{SO}_4$  (1:1). If molybdenum is indicated, the precipitate can be filtered, dissolved, and molybdenum determined photometrically. Reference should be made to the procedure for determining molybdenum by the photometric method described in Chapter 24, "Standard Methods of Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron, and Wrought Iron."

<sup>33</sup> At best, direct determinations of tungsten in high-grade metal are subject to inherent errors. Accuracy within 0.2% is all that can be expected by any method.

$$\text{Tungsten, per cent} = \frac{[A - (B - C)] \times 0.793}{D} \times 100$$

where  $A$  = grams of impure  $\text{WO}_3$  (Paragraph (c)),

$B$  = grams of insoluble residue from fusion with  $\text{Na}_2\text{CO}_3$  (Paragraph (f)),

$C$  = correction, in grams, for insoluble residue in  $\text{Na}_2\text{CO}_3$  (Paragraph (g)), and

$D$  = grams of sample used.

### TOTAL CARBON BY THE DIRECT-COMBUSTION METHOD

*Procedure.*—Determine carbon by the direct-combustion method (p. 765), with the following modification: use 1.5 to 2 g. of the sample.

### MANGANESE BY THE PERSULFATE-ARSENITE METHOD

*Apparatus.* Apparatus for Potentiometric Titration.

*Reagents.* (a) Phosphoric Acid (85%).

(b) Silver Nitrate Solution (8 g. per liter).

(c) Ammonium Persulfate Solution (250 g. per liter).

(d) Mixed Acids.—Add 100 ml. of  $\text{H}_2\text{SO}_4$  to 525 ml. of water slowly and with stirring, cool, and add 125 ml. of  $\text{H}_3\text{PO}_4$  (85%) and 250 ml. of  $\text{HNO}_3$ .

(e) Standard Potassium Permanganate Solution (0.03 N).

(f) Sulfurous Acid (6%).

(g) Standard Sodium Arsenite Solution (1 ml. = 0.0002 g. Mn).—Standardize as follows: dissolve 1 g. of electrolytic or open-hearth iron of a known, low manganese content<sup>34</sup> in 30 ml. of the acid mixture; heat until solution is complete, and boil to expel brown fumes; dilute to 100 ml. with hot water; add 20 ml. of 0.03 N  $\text{KMnO}_4$ ; and then add just enough  $\text{H}_2\text{SO}_3$  (6%) to reduce the  $\text{KMnO}_4$ ; boil again to expel brown fumes; add 10 ml. of  $\text{AgNO}_3$  (8 g. per liter) and 15 ml. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (250 g. per liter); heat to boiling, boil briskly for 1 min., and cool to 15° to 20°C. Complete the standardization in accordance with the procedure described in Paragraphs (b) and (d) or (b) and (e) below.

*Procedure.*—(a) Transfer 1 g. of the sample to a 100-ml. platinum dish provided with a platinum cover. Add 5 ml. of HF, and then add  $\text{HNO}_3$  drop by drop until the alloy is dissolved. Remove the cover and rinse with a little water. Add 5 ml. of  $\text{H}_2\text{SO}_4$  and evaporate to dense white fumes. Cool, and add 50 ml. of water. Heat at 80° to 90°C. for 15 min., while stirring occasionally, and filter into a 300-ml. Erlenmeyer flask. Wash the filter and tungstic acid well with  $\text{H}_2\text{SO}_4$  (1:99). The total volume should be approximately 125 ml.

(b) Add 3 ml. of  $\text{H}_3\text{PO}_4$  (85%), 10 ml. of  $\text{AgNO}_3$  (8 g. per liter), and 15 ml. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (250 g. per liter). Heat to boiling, and boil briskly for 1 min. Cool to 15° to 20°C., and dilute to 300 ml. with cold water.

(c) Titrate the solution in accordance with Paragraph (d) or (e).

(d) Visual Titration.—Titrate rapidly with sodium arsenite (1 m. = 0.0002 g. Mn) to a clear yellow end point that does not change upon the addition of more arsenite. If the solution is not titrated rapidly with arsenite, part of the manganese may be reoxidized by the  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  during the titration and thus yield high results.

(e) Potentiometric Titration.—Titrate rapidly with sodium arsenite (1 ml. = 0.0002 g. Mn). To titrate, bring the needle (or light-beam) on the scale, and then

<sup>34</sup> National Bureau of Standards standard sample No. 55 of ingot iron is satisfactory for this purpose.

add the sodium arsenite solution. As the end point is approached (rapid fading of the pink color) the indicator will remain stationary, or move very slowly. Continue the addition of the arsenite drop by drop until a sharp break of four to five scale divisions is obtained.

(f) Calculation.—Calculate the percentage of manganese as follows:

$$\text{Manganese, per cent} = \frac{AB}{C} \times 100$$

where  $A$  = milliliters of sodium arsenite solution required to titrate the sample,  
 $B$  = manganese equivalent of the sodium arsenite solution, in grams per milliliter,  
 and  
 $C$  = grams of sample used.

## PHOSPHORUS BY THE TARTRATE-MAGNESIA-ALKALIMETRIC METHOD

**Apparatus.** (a) **Platinum Dish.**—A flat-bottom dish shall be used, having the following dimensions: 8 cm. in diameter at the top, 7.8 cm. in diameter at the bottom, and 4 cm. in height. The dish, having a capacity of 175 ml. and weighing 58 to 60 g., shall have a wire rim at the top to provide additional stiffness. The cover shall be "dished" like a crucible cover to fit the top of the dish closely. The dish shall have a small lip to aid in pouring, and the tongue of the cover shall overlap the lip. Ordinary round-bottom dishes may be used, but in such cases the manipulation is much more difficult.

(b) **Shaking Machine.**—Any efficient shaking machine may be used.

**Reagents.** (a) **Potassium Permanganate Solution** (25 g. per liter).

(b) **Ammonium Molybdate Solution (Acidic).**—*Solution No. 1.*—Mix thoroughly 100 g. of molybdic acid (85%  $\text{MoO}_3$ ) and 240 ml. of water. Add 140 ml. of  $\text{NH}_4\text{OH}$ , while stirring vigorously. When solution is complete, filter, and add 60 ml. of  $\text{HNO}_3$ .

*Solution No. 2.*—Mix 400 ml. of  $\text{HNO}_3$  and 960 ml. of water.

When the solutions are cool, add Solution No. 1 to Solution No. 2, while stirring constantly. Add 0.1 g. of  $(\text{NH}_4)_2\text{HPO}_4$ , and allow the solution to stand at least 24 hr. before using. Use only the clear supernatant solution.

**Procedure.**—(a) Transfer 2 g. of the sample to a flat-bottom platinum dish<sup>35</sup> fitted with a platinum cover, and add 15 ml. of  $\text{HNO}_3$ ; then add 3 ml. of  $\text{HF}$  and warm gently.<sup>36</sup> When action subsides, add 3 ml. more of  $\text{HF}$ . After action subsides, boil, remove the cover, and if decomposition is not complete, add more  $\text{HF}$  and boil again. When solution is complete, wash off the cover and evaporate at a low heat to a volume of about 10 ml. Add 10 to 12 drops of  $\text{KMnO}_4$  (25 g.

<sup>35</sup> When ordinary round-bottom dishes are used, there is a greater tendency to spattering and danger of local baking or overheating, in evaporating to dense white fumes. If the separated  $\text{WO}_3$  is overheated locally, it does not dissolve readily in  $\text{NH}_4\text{OH}$ . In flat-bottom dishes, the  $\text{WO}_3$  is spread in a thin layer and heat is applied evenly over the bottom.

<sup>36</sup> For the initial treatment the  $\text{HNO}_3$  is added before the  $\text{HF}$ , and in larger proportions, in order to provide a constant excess of  $\text{HNO}_3$  to oxidize phosphorus. The procedure given takes a little longer than when the sample is treated with  $\text{HF}$  first and  $\text{HNO}_3$  is added a little at a time, but the solution is finally complete. It is necessary to keep the platinum dish covered after action begins, as the reaction is somewhat violent.

per liter),<sup>37</sup> and continue the evaporation until crusts of  $\text{WO}_3$  begin to form at the edges, that is, to a volume of about 6 ml. Add 10 ml. of  $\text{H}_2\text{SO}_4$ , and evaporate at a low heat to dense white fumes. (Strong heat causes spattering and also causes hard, over-baked crusts, which resist subsequent treatment, to form on the bottom of the dish.

(b) Cool, add 25 ml. of water, and boil (by agitating over a Bunsen flame) until all soluble salts have dissolved. Discharge the pink color, due to excess  $\text{KMnO}_4$ , by adding  $\text{H}_2\text{SO}_3$  drop by drop. The pink color may not be very evident, but the  $\text{H}_2\text{SO}_3$  shall be added, even so, to reduce higher oxides of manganese. Boil for a minute or two after adding the  $\text{H}_2\text{SO}_3$ . Add 2 g. of tartaric acid<sup>38</sup> and, when this is dissolved and the solution is cooled to a temperature of about  $50^\circ\text{C}$ ., add 40 ml. of  $\text{NH}_4\text{OH}$  (1:1). The precipitated tungstic acid should dissolve completely, giving a clear solution.

(c) The solution becomes hot from the reaction between  $\text{H}_2\text{SO}_4$  and  $\text{NH}_4\text{OH}$ . While it is still hot, add 4 g. of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  dissolved in 10 ml. of water, and transfer it from the platinum dish to a 6-oz. glass-stoppered bottle. Set the bottle in ice water, and when it is thoroughly cooled, add 4 or 5 glass beads about 6 mm. in diameter. Stopper it tightly, and shake in a shaking machine for at least 10 min. The agitation should be violent. The beads aid in starting the formation of the magnesium precipitate. After agitation, add 15 ml. of  $\text{NH}_4\text{OH}$ , return the bottle to the ice-water tank, and put into a refrigerator overnight. Phosphorus separates as magnesium-ammonium phosphate, free from tungsten, but possibly containing basic magnesium compounds. Filter through a 9-cm. paper containing a little ashless paper pulp, and wash the bottle and paper thoroughly with small portions of  $\text{NH}_4\text{OH}$  (1:20). Do not attempt to remove all the precipitate from the bottle, but remove the beads to the filter. The precipitate consists of magnesiumammonium phosphate and arsenate, together with silica and other impurities. Tin, tungsten, molybdenum, vanadium, and titanium remain in solution and are thus eliminated.

(d) Dissolve the magnesium precipitate with 40 ml. of  $\text{HNO}_3$  (1:3) and collect the filtrate in a 300-ml. Erlenmeyer flask. Wash with hot water. Add 5 g. of  $\text{NH}_4\text{NO}_3$  to the filtrate, cool to  $25^\circ\text{C}$ ., and add 60 ml. of ammonium molybdate solution. Shake, filter, and complete the determination in accordance with Paragraphs (d) to (g) of the perchloric acid-alkalimetric method for phosphorus, p. 766 above.

## SULFUR BY THE NITRIC-HYDROFLUORIC ACID-GRAVIMETRIC METHOD

**Reagents.** (a) Perchloric Acid (70%).

(b) Cinchonine Solution (125 g. per liter).—Dissolve 125 g. of cinchonine in 1 liter of  $\text{HCl}$  (1:1), and filter.

<sup>37</sup> Potassium permanganate solution is added to ensure complete oxidation of phosphorus, as in steel analysis. The color of the permanganate gradually fades in the  $\text{HF-HNO}_3$  solution, but after evaporating to fumes and adding water, the solution is usually slightly pink.

<sup>38</sup> The amount of tartaric acid is limited to 2 g., since ammonium tartrate retards the formation of the magnesia precipitate. Complete precipitation can be obtained only by brisk agitation and by keeping the solution very cold, followed by long standing in a cold place.



a free flame or in a muffle furnace. The fusion is best made over a gas flame at a low temperature until the mass has melted down quietly, when the temperature shall be increased to approximately 900°C. for about 3 min. Give the crucible a rotary motion to stir up any unattached particles of alloy adhering to the bottom or sides.

(b) When the crucible has partly cooled, and with the cover on tight, tap it several times on an iron plate to loosen the fusion in a solid cake. Transfer the cake to a dry 300-ml. porcelain casserole of good glaze, or preferably a large platinum dish. Cover, and add 80 ml. of  $\text{H}_2\text{SO}_4$  (1:1), 5 ml. of  $\text{H}_3\text{PO}_4$  (85%),<sup>39</sup> and 10 ml. of  $\text{HClO}_4$  (70%). Rinse the crucible with a little hot water, and add the rinsings to the casserole. Stir the solution well, and boil gently until the temperature increases to 195°C. Continue the heating at this temperature for 5 min. A thermometer may be suspended just below the surface of the liquid in the lip of the platinum dish or casserole. At the temperature specified, fumes of  $\text{HClO}_4$  will be freely evolved.

(c) Allow the mass to cool somewhat, and add 200 ml. of warm tartaric acid (80 g. per liter). Heat at a temperature of 60° to 70°C., while stirring occasionally, until all ferric sulfate has dissolved. Filter, using moderate suction, on an 11-cm. paper containing some ashless paper pulp, and wash thoroughly with tartaric acid (50 g. per liter).

(d) Ignite in platinum, first at a low temperature and finally at 1100° to 1150°C. for 30 min. Cool in a desiccator and weigh.

(e) Add several drops of  $\text{H}_2\text{SO}_4$  and 1 or 2 ml. of  $\text{HF}$ , and heat until white fumes are no longer evolved. Ignite at 800°C. for 10 min., cool, and weigh. The loss in weight represents  $\text{SiO}_2$ .

(e) Blank.—Make a blank determination, using the same apparatus and procedure and the same amounts of all reagents.

(f) Calculation.—Calculate the percentage of silicon as follows:

$$\text{Silicon, per cent} = \frac{(A - B) \times 0.4672}{C} \times 100$$

where  $A$  = grams of  $\text{SiO}_2$ ,

$B$  = correction for blank, in grams, and

$C$  = grams of sample used.

### THE SODIUM HYDROXIDE TITRATION (VOLUMETRIC) METHOD

**Reagents.** (a) Nitric Acid Solution of Potassium Nitrate (Saturated).—Saturate  $\text{HNO}_3$  with  $\text{KNO}_3$ , at 20°C.

(b) Aqueous Solution of Potassium Nitrate (Saturated).—Saturate water with  $\text{KNO}_3$ , at 20°C.

(c) Phenolphthalein Indicator Solution (10 g. per liter).

(d) Standard Sodium Hydroxide Solution (0.10  $N$ ).

**Procedure.**—(a) Transfer 1 g. of the sample to a 300-ml. platinum dish; add 30 ml. of  $\text{HNO}_3$  saturated with  $\text{KNO}_3$  and 5 ml. of  $\text{HF}$ . Heat gently until dissolution is complete and fumes have ceased to evolve. Remove from the heat and cool the dish and contents to 15° to 20°C. in ice water.

(b) Prepare a filter using an 11-cm., ashless, rapid paper, reinforced with a 5.5-

<sup>39</sup> The function of the  $\text{H}_3\text{PO}_4$  is to hold most of the tungsten in solution, and thus to effect its separation from the silica. Fuming with  $\text{HClO}_4$ , as specified, will break up any soluble silicophosphotungstate.

(c) Cool, and transfer to the 500-ml. distillation flask (Fig. 25-2). Add 200 ml. of HCl, 20 g. of  $\text{FeSO}_4$ , 10 ml. of HBr (48%), and several pea-size pieces of coke, and connect the stopper carrying the trap and delivery tube shown.<sup>41</sup> The outlet of the delivery tube should dip about 1 in. below the surface of 200 ml. of cold water

contained in an 800-ml. beaker. Heat the solution in the 500-ml. flask to boiling and continue to boil until approximately 200 ml. have been distilled over (which generally coincides with the beginning of objectionable bumping). Remove the distillate.

(d) By the procedure described in Paragraphs (a) to (c), the arsenic is separated from any other elements likely to interfere with the method. To the distillate containing the arsenic in the form of arsenious chloride,  $\text{AsCl}_3$ , add a slight excess of  $\text{NH}_4\text{OH}$ , using litmus paper as indicator, and keeping the solution cool. Add sufficient HCl (1:1) to render the solution slightly acid. Then add to the cold, slightly acid solution 15 g. of  $\text{NaHCO}_3$ , 0.3 g. of KI, and several milliliters of starch solution (10 g. per liter) and titrate with 0.03 *N* iodine to the appearance of the blue color. If desired, 0.03 *N*  $\text{KIO}_3$  may be used for the titration in place of the 0.03 *N* iodine solution, adding 2 to 3 g. of KI instead of 0.3 g. before the titration.

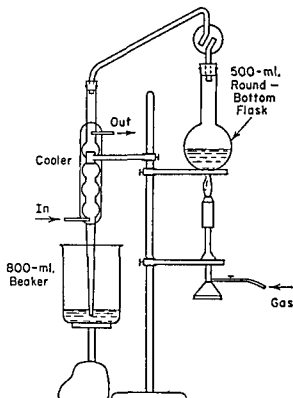


FIG. 25-2. Apparatus for Determination of Arsenic by Distillation.

(e) Blank.—Make a blank determination, following the same procedure and using the same amounts of all reagents.

(f) Calculation.—Calculate the percentage of arsenic as follows:

$$\text{Arsenic, per cent} = \frac{(A - B)C \times 0.0375}{D} \times 100$$

where *A* = milliliters of iodine solution required for titration of the sample,

*B* = milliliters of iodine solution required for titration of the blank,

*C* = normality of the iodine solution, and

*D* = grams of sample used.

## COPPER

**Reagents.** (a) Tartaric Acid Wash Solution.—Dissolve 10 g. of tartaric acid in 1 liter of  $\text{H}_2\text{SO}_4$  (1:99) and saturate with  $\text{H}_2\text{S}$ .

(b) Potassium Hydroxide-Potassium Sulfide Solution.—Saturate 250 ml. of KOH (100 g. per liter) with  $\text{H}_2\text{S}$  and then add 750 ml. of KOH (100 g. per liter).

<sup>41</sup> Any rubber connections in the apparatus used should be made from "sulfur-free" rubber as sulfur would be extracted from ordinary rubber and would pass into the distillate as  $\text{H}_2\text{S}$ , which would react with the iodine and cause high results.

(c) Potassium Hydroxide-Potassium Sulfide Wash Solution.—Dilute 100 ml. of KOH-K<sub>2</sub>S solution to 1 liter.

(d) Acetic Acid (99.5%).

(e) Potassium Iodide Solution (300 g. per liter).

(f) Standard Sodium Thiosulfate Solution (1 ml. = 0.0005 g. Cu, approximately 0.008 N).—Allow to stand several days before standardizing. To standardize, dissolve 0.5 g. of copper in 10 ml. of HNO<sub>3</sub> and dilute to 500 ml. Take 25 ml. of this solution, withdrawn by means of a calibrated pipet, and titrate as described in Paragraph (h) below.

(g) Starch Solution (10 g. per liter).—Make a paste of 1 g. of soluble (or arrow-root) starch in about 5 ml. of water and add to 100 ml. of boiling water. Cool, add 5 g. of KI, and stir until the KI is dissolved. Prepare fresh as needed.

*Procedure.*—(a) Transfer 5 g. of the sample to a 300-ml. platinum dish provided with a platinum cover, and add 50 ml. of HNO<sub>3</sub>. Add HF, a little at a time, with occasional heating, until the alloy is dissolved. Rinse the cover with water, and evaporate to approximately 25 ml. Add 35 ml. of H<sub>2</sub>SO<sub>4</sub>, and continue the evaporation to dense white fumes. Cool, and transfer to a 600-ml. beaker. Rinse the dish successively with hot NH<sub>4</sub>OH (1:1), 5 ml. of hot water, 5 ml. of hot H<sub>2</sub>SO<sub>4</sub> (1:1), and finally with 10 ml. of hot water. Dilute with water to 100 ml., add 20 g. of tartaric acid and an excess (about 10 ml.) of NH<sub>4</sub>OH, and heat just short of boiling for several minutes. Add an excess of 2 ml. of H<sub>2</sub>SO<sub>4</sub> (1:1) for each 100 ml. of solution, and pass a brisk stream of H<sub>2</sub>S into the solution for at least 30 min. Filter on an 11-cm. paper containing a little ashless paper pulp, and wash thoroughly with tartaric acid wash solution.

(b) Return the paper and sulfides to the beaker in which the precipitation was made, and add 50 ml. of KOH-K<sub>2</sub>S solution. Add 1 g. of Na<sub>2</sub>O<sub>2</sub>, and gradually heat to boiling over a period of 5 min., while stirring occasionally. Dilute with an equal volume of water, filter into a 400-ml. beaker, and wash with KOH-K<sub>2</sub>S wash solution. Reserve the filtrate for the determination of tin and antimony (described below, on pp. 800 and 802).

(c) Wash the CuS precipitate 12 to 15 times with H<sub>2</sub>S wash solution and ignite in porcelain at a low temperature (520° to 550°C., preferably in a muffle furnace) until all carbon is destroyed. Cool and transfer the contents of the crucible to a 300-ml. Erlenmeyer flask. Add 5 to 6 ml. of HNO<sub>3</sub> (1:1) to the crucible, warm gently, and pour upon the residue in the flask. Rinse the crucible with a little water, and warm the flask and contents until the copper oxide is dissolved. Carefully evaporate the solution to a volume of 2 to 3 ml. in order to expel most of the free acid. Then add NH<sub>4</sub>OH until the solution just reacts alkaline to litmus.

(d) Complete the determination by the electrolytic method (Paragraphs (e) to (g)) or the iodide method (Paragraphs (h) and (i)).

*Electrolytic Method.*—(e) Transfer the ammoniacal solution (Paragraph (c)) to a 250-ml. beaker, neutralize with H<sub>2</sub>SO<sub>4</sub> (1:1), add an excess of 5 ml. of H<sub>2</sub>SO<sub>4</sub> (1:1), and then add 4 ml. of HNO<sub>3</sub> (1:1). Dilute the solution to 200 ml. Adjust the anode and weighed cathode, cover the beaker with split watch glasses, and electrolyze at a current density of 0.5 amp. per sq. dm. until the solution becomes colorless (about 2 hr.). Rinse the cover glasses and the exposed stems of the electrodes and sides of the beaker. Continue the electrolysis for 30 min. and test for complete deposition (0.3 to 0.5 ml. of the electrolyte should not give a brown color with 0.3 to 0.5 ml. of freshly prepared H<sub>2</sub>S water).

(f) When deposition is complete, continue the current and lower the beaker while rinsing the cathode with water from a wash bottle.<sup>42</sup> When the cathode is free from electrolyte, turn off the current and detach the cathode. Dip it in two successive baths of ethanol or methanol, shake off the excess, and dry in an oven at 110°C. for 3 to 5 min. Cool in a desiccator, and weigh the deposit as metallic copper.<sup>43</sup>

(g) Calculation.—Calculate the percentage of copper as follows:

$$\text{Copper, per cent} = \frac{.1}{B} \times 100$$

where .1 = grams of copper, and

B = grams of sample used.

**Iodide Method.**—(h) Dilute the solution to 40 ml., add  $\text{NH}_4\text{OH}$  in slight excess, and boil until the odor of ammonia is very faint. Add 1 ml. of acetic acid (99.5%) and continue boiling for 1 min. Cool to room temperature, and add 5 ml. of KI (300 g. per liter) and 2 ml. of starch solution (10 g. per liter). Titrate the liberated iodine with  $\text{Na}_2\text{S}_2\text{O}_3$  (1 ml. = 0.0005 g. Cu) to the disappearance of the blue color.

(i) Calculation.—Calculate the percentage of copper as follows:

$$\text{Copper, per cent} = \frac{AB}{C} \times 100$$

where A = milliliters of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required for titration,

B = copper equivalent of the  $\text{Na}_2\text{S}_2\text{O}_3$  solution, in grams per milliliter, and

C = grams of sample used.

## TIN

**Apparatus.** Apparatus for Reduction of Tin.—When tin is to be reduced to the stannous state and determined by titration with standard iodine or iodate solution, air must be excluded during the reduction and titration to prevent oxidation of the stannous tin. This is usually accomplished by keeping the solution under a blanket of gaseous  $\text{CO}_2$ . It may be accomplished in a variety of ways. One of the simplest methods is by means of the apparatus shown in Fig. 25-3 in which the reduction of the tin solution is made in a flask capped with a rubber stopper containing an L-shaped siphon tube. When reduction is complete, the end of the siphon shall be dipped into a saturated solution of  $\text{NaHCO}_3$  and set aside to cool. When cool, the stopper is removed and the solution titrated.

**Reagents.** (a) Hydrogen Sulfide Wash Solution.—Saturate HCl (1:99) with  $\text{H}_2\text{S}$ .

(b) Hydrogen Sulfide-Oxalic Acid Wash Solution.—Saturate  $\text{H}_2\text{SO}_4$  (1:199) with  $\text{H}_2\text{S}$  and dissolve in the solution a few crystals of oxalic acid for each 100 ml.

(c) Ferric Sulfate Solution (10 g. per liter).

(d) Test Lead.

(e) Starch Solution (10 g. per liter).—This solution shall be freshly prepared as needed.

<sup>42</sup> In work of high accuracy, recover traces of copper in the electrolyte by the sulfide-colorimetric method.

<sup>43</sup> Deposits of copper may be removed as follows: immerse the cathode in  $\text{HNO}_3$  (1:1); rinse with water; boil with fresh  $\text{HNO}_3$  for 5 to 10 min.; and rinse with water; ignite strongly for 10 to 25 min. over one or two large Meker burners.

(f) **Standard Iodine Solution** (1 ml. = 0.002 g. Sn, approximately 0.03 *N*).—To standardize, dissolve 0.02 g. of tin in HCl, and then reduce the tin with lead and titrate with the iodine solution as described in the procedure below. For the small amounts of tin involved, the theoretical tin equivalent as based on standardization against arsenious oxide may be used.

(g) **Standard Potassium Iodate Solution** (1 ml. = 0.002 g. Sn, approximately 0.03 *N*).—To standardize, dissolve 0.02 g. of tin in HCl, and then reduce the tin with lead and titrate with the  $\text{KIO}_3$  solution as described in the procedure below. For the small amounts of tin involved, the theoretical tin equivalent as based on standardization against sodium oxalate may be used.

**Procedure.**—(a) Add HCl to the filtrate reserved from the determination of copper until the solution is acid, and then add 1 ml. of HCl in excess per 100 ml. of solution. Filter and wash with  $\text{H}_2\text{S}$  wash solution.

(b) Transfer the paper and sulfides to a 400-ml. beaker, treat with 10 ml. of HCl, and add  $\text{KClO}_3$ , a few crystals at a time, while warming the solution to 35° to 40°C. Dilute to 200 ml. and boil gently to expel chlorine. Add 5 g. of oxalic acid, heat to 50° to 70°C., and pass in a rapid stream of  $\text{H}_2\text{S}$  for 20 to 30 min. Filter, and wash thoroughly with  $\text{H}_2\text{S}$ -oxalic acid wash solution.

Reserve the filter paper and precipitate for the determination of antimony.

(c) Add 5 ml. of  $\text{H}_2\text{SO}_4$  to the filtrate, and evaporate to dense white fumes. Cool somewhat, and dilute with 100 ml. of water. Add 50 ml. of  $\text{Fe}_2(\text{SO}_4)_3$  (10 g. per liter) and heat to boiling. Stir vigorously and add  $\text{NH}_4\text{OH}$  (1:1) until the solution is alkaline, and then add 3 to 5 ml. in excess. Let settle, filter, and wash with hot water.

(d) Dissolve the precipitate in 80 ml. of hot HCl (1:1) and wash the filter with hot water, collecting the solution (not over 150 ml. in volume) in a 500-ml. Erlenmeyer flask.

(e) Add 1 to 2 g. of test lead and close the flask with a one-hole rubber stopper carrying a bent delivery tube (Fig. 25-3). Boil gently for 20 min. At the end of this period immerse the end of the delivery tube in a small beaker containing about 50 ml. of saturated  $\text{NaHCO}_3$  solution.

(f) Remove the flask from the hot plate, keeping the delivery tube immersed in the  $\text{NaHCO}_3$  solution, and cool in a stream of cold water. When cool, remove the stopper, add 5 ml. of starch solution (10 g. per liter), and titrate with 0.03 *N* iodine to a permanent blue color. If desired, 0.03 *N*  $\text{KIO}_3$  may be used for the titration in place of the 0.03 *N* iodine solution, adding 2 to 3 g. of KI before the titration.

(g) **Blank.**—Make a blank determination, following the same procedure and using the same amounts of all reagents.

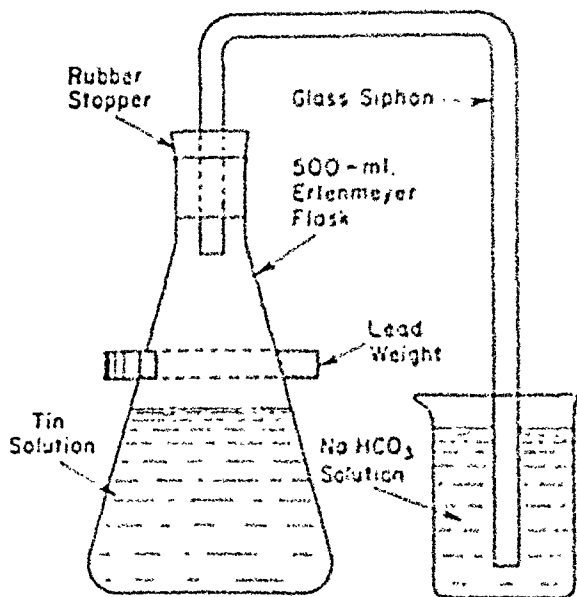


FIG. 25-3. Apparatus for Reduction of Tin.

(e) **Ferric Phosphate Solution.**—Dissolve 100 g. of  $\text{Fe}_2(\text{SO}_4)_3$  in 1 liter of water to which 150 ml. of  $\text{H}_3\text{PO}_4$  (85%) and 20 ml. of  $\text{H}_2\text{SO}_4$  (1:1) have been added. Add  $\text{KMnO}_4$  (25 g. per liter) until the solution is just tinted pink, due to the excess of  $\text{KMnO}_4$ .

(f) **Standard Potassium Permanganate Solution** (0.1 N).

(g) **Sodium Thiocyanate Solution** (50 g. per liter).

(h) **Stannous Chloride Solution.**—Transfer 350 g. of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  to a 500-ml. Erlenmeyer flask, add 200 ml. of  $\text{HCl}$  (1:1), and boil gently until solution is practically complete. Transfer the solution to a 1-liter bottle, and dilute to 1 liter with freshly boiled water. Add a few pieces of metallic tin, and stopper.

(i) **Ferric Sulfate Solution.**—Dissolve 80 g. of  $\text{Fe}_2(\text{SO}_4)_3$  in 1 liter of  $\text{H}_2\text{SO}_4$  (1:1).

(j) **Standard Molybdenum Solution** (1 ml. = 0.0005 g. Mo).

(k) **Isopropyl Ether.**—Shake isopropyl ether in a separatory funnel with 100 ml. of  $\text{H}_2\text{SO}_4$  (1:9), 10 ml. of  $\text{Fe}_2(\text{SO}_4)_3$  solution (Paragraph (i)), 10 ml. of  $\text{NaCNS}$  (50 g. per liter), and 10 ml. of  $\text{SnCl}_2$  solution (Paragraph (h)).

**Procedure.**—(a) Transfer 0.5 g. of the sample to a 150-ml. beaker, cover, add 10 ml. of  $\text{HNO}_3$  (1:3), and warm to complete solution. If the sample dissolves with difficulty, add a drop or two of  $\text{HF}$ . When reaction is complete, cautiously add 10 ml. of  $\text{H}_2\text{SO}_4$  (1:1) and evaporate to dense white fumes. Cool, add 40 ml. of water, and warm until all salts have dissolved. Rinse and remove the cover. Filter, and wash the paper and residue 12 to 15 times with hot water, 3 to 4 times with hot  $\text{NH}_4\text{OH}$  (1:3), and finally 4 to 5 times with hot water, the washings being allowed to run into the main filtrate. Discard the residue.

(b) Cool the filtrate, add  $\text{NH}_4\text{OH}$  until it is difficult to avoid a red tint, and heat the slightly acid solution to boiling. Slowly pour the solution, while stirring vigorously, into 75 ml. of nearly boiling  $\text{NH}_4\text{OH}$  (1:5) in a 600-ml. beaker. Rinse the beaker that held the filtrate with a little water and then with a little hot  $\text{NH}_4\text{OH}$  (1:5), and add the rinsings to the main solution. Add a little paper pulp, filter into a 600-ml. beaker, and wash the precipitate with hot water. Set the filtrate aside.

(c) Dissolve the precipitate in a slight excess of hot  $\text{H}_2\text{SO}_4$  (1:4), nearly neutralize with  $\text{NH}_4\text{OH}$ , and pour into  $\text{NH}_4\text{OH}$  (1:5) as before. Filter into the reserved filtrate (Paragraph (b)). Dissolve the precipitate and repeat the operation.

(d) Dissolve the precipitate of  $\text{Fe}(\text{OH})_3$  in a slight excess of hot  $\text{H}_2\text{SO}_4$  (1:4), wash the filter with hot water, and reserve the filtrate for further treatment.

(e) Add 3 g. of powdered tartrac acid to the combined ammoniacal filtrates (Paragraph (c)), stir until dissolved, and saturate the solution with  $\text{H}_2\text{S}$ . If a precipitate appears, filter, and wash with  $(\text{NH}_4)_2\text{S}$  wash solution. Warm the filtrate, cover the beaker, and add  $\text{H}_2\text{SO}_4$  (1:1) until the solution contains 10 ml. of  $\text{H}_2\text{SO}_4$  in excess for each 100 ml. of solution. Heat the solution just to boiling and let stand at the side of a steam bath (about  $40^\circ\text{C}$ .) for 15 min., until the precipitate has settled. Filter, and wash thoroughly with tartaric acid wash solution. Reserve the filtrate.

(f) Transfer the paper and precipitate ( $\text{MoS}_3$ ) to the original 600-ml. beaker (Paragraph (b)). Place a glass stirring rod in the beaker, cover, and add 6 ml. of  $\text{H}_2\text{SO}_4$  and 10 ml. of  $\text{HNO}_3$ . Cautiously heat to dense white fumes. Let cool, add 5 ml. of  $\text{HNO}_3$ , again heat to dense white fumes, and repeat the treatment until the yellow color due to organic matter has disappeared. Cool, rinse, and remove the cover. Rinse the inside of the beaker, and add  $\text{KMnO}_4$  (25 g. per liter) very cautiously until a permanent red tint is obtained. Again evaporate to dense

white fumes. Cool, and add 75 ml. of water. Boil for a few minutes, add 2 g. of 20-mesh zinc, and continue the boiling until any copper has been reduced to the metallic form. Filter through a 9-cm. paper and wash with hot water. Add a slight excess of  $\text{KMnO}_4$  (25 g. per liter).

(g) If the Jones reductor has been standing idle, pass 100 ml. of warm ( $40^\circ$  to  $50^\circ\text{C}.$ )  $\text{H}_2\text{SO}_4$  (5:95) through it and then a little cold water. Discard the wash solution. Add 35 ml. of ferric phosphate solution to the receiver, and then enough water so that the tip of the reductor dips well beneath the surface of the solution when the receptacle is connected with the reductor. Draw the cool (about  $20^\circ\text{C}.$ ) solution of molybdenum, which should be about 100 ml. in volume and contain about 5 ml. of  $\text{H}_2\text{SO}_4$ , through the reductor, while gently swirling the solution in the receiving flask. Just before the surface of the liquid reaches the zinc, add 50 ml. of cold  $\text{H}_2\text{SO}_4$  (5:95) and finally rinse twice more by adding 50 ml. of water each time just before the surface of the solution reaches the zinc. Close the stop-cock while a portion of the last washing solution remains in the reductor funnel. Disconnect and raise the reductor as a little water is allowed to run through the stem and rinse the outside of the stem. Titrate the solution with 0.1 *N*  $\text{KMnO}_4$ .

(h) Blank.—Make a blank determination, following the procedure described in Paragraphs (a) to (g).

(i) Boil down the filtrate reserved in accordance with Paragraph (e) to a volume of about 75 ml., and combine with the solution reserved in accordance with Paragraph (d). Add 1 to 2 g. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , boil down to a volume of 100 ml., and cool to  $15^\circ\text{C}.$  Add sufficient  $\text{H}_2\text{SO}_4$  (1:1) to give a solution containing approximately 10%  $\text{H}_2\text{SO}_4$  by volume. The sodium-molybdenum thiocyanate amber to reddish brown color is best developed in a solution containing 10%  $\text{H}_2\text{SO}_4$  by volume.

(j) Cool to  $25^\circ\text{C}.$ , and transfer to a 500-ml. separatory funnel. Add 10 ml. of  $\text{NaCNS}$  (50 g. per liter) and 10 ml. of  $\text{SnCl}_2$  solution. Stopper and shake vigorously for several minutes. Add 50 ml. (or more if needed) of isopropyl ether,<sup>44</sup> and shake for 1 to 2 min. longer. Allow the extract to separate, draw off the lower layer, and set it aside. Transfer the extract to a 150-ml. Nessler, Julian, or similar colorimeter tube. Return the lower acid layer to the separatory funnel and shake again with approximately 25 ml. of ether. Should the upper layer have an amber to reddish brown color, add it to the solution in the colorimeter tube.

(k) Prepare a color standard containing approximately the same concentration of molybdenum as the sample solution. Transfer 25 ml. of  $\text{Fe}_2(\text{SO}_4)_3$  solution to a 250-ml. separatory funnel containing 10 ml. of cold water, and add molybdenum solution (1 ml. = 0.0005 g. Mo) from a buret. Cool the solution to about  $25^\circ\text{C}.$ , and proceed as described in Paragraph (j).

(l) Allow both the sample solution and the color standard to stand for several minutes before comparing. Dilute the darker of the two solutions with isopropyl ether, and mix thoroughly until the sample and the standard match exactly. The colorimetric determination is limited to solutions containing not more than 0.05 mg. of molybdenum per milliliter.

(m) Calculation.—Calculate the percentage of molybdenum as follows:

$$\text{Molybdenum per cent} = \frac{[(A - B)C \times 0.032] \times D}{E} \times 100$$

<sup>44</sup> Butyl acetate prepared in the same manner may be used instead of the isopropyl ether, but the isopropyl ether is preferred.

where  $A$  = milliliters of  $\text{KMnO}_4$  solution required for titration of the reduced molybdenum solution (Paragraph (g)),

$B$  = milliliters of  $\text{KMnO}_4$  solution required for titration of the blank (Paragraph (h)),

$C$  = normality of the  $\text{KMnO}_4$  solution,

$D$  = grams of molybdenum determined colorimetrically (Paragraph (i)), and

$E$  = grams of sample used.

### TOTAL CARBON BY THE DIRECT-COMBUSTION METHOD

**Procedure.**—Determine carbon by the direct-combustion method (p. 765), with the following modifications: (1) use 1.5 to 2 g. of the sample; (2) it is advisable to use an accelerator such as 40-mesh ingot iron or red lead,<sup>45</sup> particularly with low-carbon alloys. If accelerators are added, a proper correction for the blank should be obtained; (3) use a furnace temperature of 1100° to 1200°C.; and (4) because of the high sulfur maximum, special provision must be made for the removal of oxides of sulfur in the exit gases. This can be done (1) by passing the gases through platinized silica gel heated to 500°C. and then through a column of ironized asbestos, or (2) by passing through a strong solution of chromic acid or  $\text{KMnO}_4$  and then through a desiccant such as anhydrous  $\text{Mg}(\text{ClO}_4)_2$ .

### SULFUR BY THE NITRIC ACID-GRAVIMETRIC METHOD

**Reagents.** (a) Barium Chloride Solution (100 g. per liter).

(b) Barium Chloride Wash Solution.—Dilute 10 ml. of  $\text{BaCl}_2$  (100 g. per liter) to 1 liter with  $\text{HCl}$  (1:99).

(c)  $\alpha$ -Benzoinoxime, Acetone Solution (50 g. per liter).

(d)  $\alpha$ -Benzoinoxime Wash Solution.—Dilute 5 ml. of the acetone solution of  $\alpha$ -benzoinoxime to 1 liter with cold  $\text{HCl}$  (1:99).

**Procedure.**—(a) Transfer 2 to 5 g. of the sample to a 500-ml. casserole, and dissolve it in 30 to 75 ml. of  $\text{HNO}_3$ . The reaction is likely to be very rapid and the acid should be added cautiously to the covered casserole, preferably kept cooled by immersion in ice water. It may be found necessary to add the sample in small portions to the cooled acid.

(b) Add 30 ml. of  $\text{HCl}$  and 1 g. of  $\text{Na}_2\text{CO}_3$  and evaporate to dryness on a sand or steam bath. Add 30 ml. more of  $\text{HCl}$ , evaporate to dryness again, and bake for 30 min. at 110°C. Add 25 to 50 ml. of  $\text{HCl}$  and, when solution is complete, dilute with water and filter to remove  $\text{SiO}_2$ .

(c) Evaporate the filtrate to 15 to 25 ml., to expel most of the free acid, and dilute to 100 ml. with warm water. Add a little paper pulp, filter, and wash, first with  $\text{HCl}$  (1:99), and then with water.

(d) Dilute the filtrate to 200 ml., add 20 ml. of  $\text{BaCl}_2$  (100 g. per liter), and stir vigorously for several minutes. Allow to stand overnight at room temperature and filter on a close-texture paper. Wash the paper and  $\text{BaSO}_4$  from 18 to 20 times with cold  $\text{BaCl}_2$  wash solution.

<sup>45</sup> Red lead to be used for this purpose should first be heated in an atmosphere of oxygen in an open porcelain dish, with frequent stirring, at 500° to 550°C. for 15 to 24 hr.; then cooled in a desiccator and transferred to a tightly stoppered bottle, preferably one with a ground-glass stopper. When red lead is employed, the determination should be completed promptly in order not to expose the red lead to the atmosphere any longer than necessary, as it readily absorbs  $\text{CO}_2$  from the air.



ring constantly. Add 0.1 g. of  $(\text{NH}_4)_2\text{HPO}_4$ , and allow the solution to stand at least 24 hr. before using. Use only the clear supernatant solution.

(f) Potassium Nitrate Solution (10 g. per liter).—Dissolve 10 g. of  $\text{KNO}_3$  in water and dilute to 1 liter.

*Procedure.* (a) Transfer 0.5000 g. of the sample (all of which shall pass a No. 100 (149- $\mu$ ) sieve) to a 100-ml. platinum dish, cover, and add 10 ml. of  $\text{H}_2\text{SO}_4$  (1:1), 5 ml. of HF, and sufficient  $\text{HNO}_3$  dropwise to effect dissolution. Remove, rinse the cover and sides of the dish, and evaporate just to dryness on a sand bath.

(b) Cool, add 50 ml. of  $\text{H}_2\text{SO}_4$  (1:9), and stir well. Digest and transfer to a 400-ml. beaker, rinsing the dish with 50 ml. of HCl (1:1) and a little water. Add 50 ml. of HCl (1:1), heat until salts are in solution, cool to 20°C., and add a little paper pulp followed by a slight excess of cold, freshly prepared cupferron solution.

(c) Stir well, then filter through a 12.5-cm. medium paper (to which a little paper pulp has been added) into an 800-ml. beaker, and wash 18 to 20 times with cold cupferron wash solution. Discard the precipitate.

(d) To the filtrate add 25 ml. of  $\text{HNO}_3$  and 10 ml. of  $\text{HClO}_4$  (Caution) and evaporate to dense white fumes to ensure complete destruction of all organic matter. Cool, add 150 ml. of  $\text{H}_2\text{O}$ , heat to boiling, and filter through a 9-cm. medium paper into a 400-ml. beaker. Wash the paper 10 times with hot water.

(e) Add 10 g. of  $\text{NH}_4\text{Cl}$ , 5 drops of bromocresol purple, and  $\text{NH}_4\text{OH}$  (1:1), until the color of the solution just changes to purple. Boil for 1 min., allow the precipitate to settle, and filter on an 11-cm. medium paper to which a little paper pulp has been added. Wash 10 times with hot  $\text{NH}_4\text{Cl}$  wash solution. Wash the precipitate and paper pulp back into the beaker, add 100 ml. of HCl (1:9) and 10 g. of  $\text{NH}_4\text{Cl}$ , heat to boiling, and repeat the precipitation with  $\text{NH}_4\text{OH}$ , filtering on the same paper and washing as before.

(f) Ignite the precipitate in a platinum crucible, first at a low temperature to burn off the paper, and finally at 1150°C. to constant weight. Cover the crucible when removing from the furnace, cool in a desiccator, and weigh as soon as possible as  $\text{Al}_2\text{O}_3$  plus  $\text{P}_2\text{O}_5$ .

(g) Fuse the ignited precipitate with 5 g. of  $\text{Na}_2\text{CO}_3$  at 1100°C. for 30 min. Dissolve the cold melt in 50 ml. of warm water and acidify with  $\text{HNO}_3$ , adding 2 to 3 ml. in excess. Transfer to a 250-ml. Erlenmeyer flask and add 40 ml. of molybdate solution. Complete the determination for phosphorus as described in Paragraphs (e) and (f) of the section on phosphorus by the perchloric acid-alkalimetric method, above. Calculate any phosphorus found to  $\text{P}_2\text{O}_5$  as follows:

$$\text{P} \times 2.295 = \text{P}_2\text{O}_5$$

(h) Calculation.—Calculate the percentage of aluminum as follows:

$$\text{Aluminum, per cent} = \frac{(A - B) \times 0.5291}{C} \times 100$$

where  $A$  = grams of  $\text{Al}_2\text{O}_3$  plus  $\text{P}_2\text{O}_5$ ,

$B$  = grams of  $\text{P}_2\text{O}_5$ , and

$C$  = grams of sample used.

## SILICON BY THE SULFURIC ACID METHOD

*Principle of Method.*—The sample is fused with  $\text{Na}_2\text{O}_2$  in an iron crucible, the melt transferred to :  
 1 acidified with  $\text{H}_2\text{SO}_4$ . The solution is evapo-

(c) Ammonium Sulfide Wash Solution.—Dissolve 20 g. of  $\text{NH}_4\text{Cl}$  and 10 g. of ammonia tartrate in 500 ml. of water. Add  $\text{NH}_4\text{OH}$  in slight excess, dilute to 1 liter, and saturate with  $\text{H}_2\text{S}$ .

(d) Cupferron Solution (60 g. per liter).

(e) Cupferron Wash Solution.—Dilute 20 ml. of cupferron solution (60 g. per liter) to 1 liter with cold  $\text{H}_2\text{SO}_4$  (1:9).

(f) Ammonium Phosphate Solution (160 g. per liter).—Dissolve 160 g. of  $(\text{NH}_4)_2\text{HPO}_4$  in water and dilute to 1 liter. Filter before using.

(g) Boric Acid Solution (40 g.  $\text{H}_3\text{BO}_3$  per liter).—Dissolve 40 g. of  $\text{H}_3\text{BO}_3$  in water and dilute to 1 liter.

(h) Ammonium Nitrate Solution (50 g. per liter).—Dissolve 50 g. of  $\text{NH}_4\text{NO}_3$  in water and dilute to 1 liter.

(i) Standard Ferrous Ammonium Sulfate Solution (0.2 N).—Dissolve 7.85 g. of  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  in 500 ml. of cold  $\text{H}_2\text{SO}_4$  (5:95), and dilute to 1 liter with  $\text{H}_2\text{SO}_4$  (5:95). Standardize using 10 ml. of 0.1 N  $\text{K}_2\text{Cr}_2\text{O}_7$ .

*Procedure.*—(a) Transfer 0.5000 g. of the sample (all of which shall pass a No. 100 (149- $\mu$ ) sieve) to a platinum dish of 100-ml. capacity (or larger). Cover and add 15 ml. of  $\text{H}_2\text{SO}_4$  (1:1), 5 ml. of HF (10 ml. if silicon is over 10%), and sufficient  $\text{HNO}_3$  dropwise, to effect dissolution. Remove, and rinse the cover and sides of the dish. Evaporate just to dryness on a sand bath and cool. Add 30 ml. of  $\text{H}_2\text{SO}_4$  (1:4), stir well, heat for a few minutes, and transfer to a 100-ml. beaker. Heat until all sulfates have dissolved, dilute to 200 ml., add 20 ml. of tartaric acid solution, and pass in a brisk stream of  $\text{H}_2\text{S}$  for at least 20 min.

(b) If a precipitate forms, filter through a 9-cm., medium paper, containing paper pulp, into a 600-ml. beaker. Wash about 20 times with  $\text{H}_2\text{S}$  wash solution. To the filtrate, or to the clear solution if filtration was unnecessary, add paper pulp and  $\text{NH}_4\text{OH}$  in slight excess. Pass a brisk stream of  $\text{H}_2\text{S}$  through the solution for at least 7 min., and filter, as soon as the precipitate settles, through an 11-cm., medium paper, containing paper pulp, into an 800-ml. beaker. Wash the paper and precipitate about 20 times with  $(\text{NH}_4)_2\text{S}$  wash solution. Reserve the paper and precipitate.

(c) Boil the filtrate for about 10 min.; then add 25 ml. of  $\text{H}_2\text{SO}_4$  (1:1) and boil down to 150 ml. Cool to 15° to 20°C.; then add a little paper pulp and a slight excess of a cold, freshly prepared solution of cupferron. Stir well, and filter on two superimposed 11-cm., medium papers containing a little paper pulp, supported in a Büchner funnel, using moderate suction. Wash about 20 times with cold cupferron wash solution.

(d) Ignite the paper and precipitate in a weighed platinum dish, first at a low temperature to burn off carbonaceous matter, and finally at 1050° to 1100°C. for 20 min. Cool and weigh as  $\text{TiO}_2$  plus  $\text{ZrO}_2$  plus  $\text{V}_2\text{O}_5$ . Fuse the oxides with about 5 g. of  $\text{K}_2\text{S}_2\text{O}_7$ , and dissolve the cold melt in 70 ml. of  $\text{H}_2\text{SO}_4$  (1:9). Add 5 ml. of  $\text{H}_2\text{O}_2$  and 25 ml. of filtered  $(\text{NH}_4)_2\text{HPO}_4$  solution, and allow to stand overnight at a temperature of 70°C., stirring occasionally.

(e) Filter on an 11-cm., medium paper, containing paper pulp, wash about 20 times with HCl (2:98) and finally about 5 times with  $\text{NH}_4\text{NO}_3$  solution. Ignite in platinum, first at a temperature not over 600°C. until the carbonaceous matter has burned off, and finally at 1050° to 1100°C. to constant weight. Cool and weigh as  $\text{ZrP}_2\text{O}_7$ . Calculate to  $\text{ZrO}_2$  as follows:

$$\text{ZrP}_2\text{O}_7 \times 0.4647 = \text{ZrO}_2$$

ring constantly. Add 0.1 g. of  $(\text{NH}_4)_2\text{HPO}_4$ , and allow the solution to stand at least 24 hr. before using. Use only the clear supernatant solution.

(f) Potassium Nitrate Solution (10 g. per liter).—Dissolve 10 g. of  $\text{KNO}_3$  in water and dilute to 1 liter.

*Procedure.* (a) Transfer 0.5000 g. of the sample (all of which shall pass a No. 100 (149- $\mu$ ) sieve) to a 100-ml. platinum dish, cover, and add 10 ml. of  $\text{H}_2\text{SO}_4$  (1:1), 5 ml. of  $\text{HF}$ , and sufficient  $\text{HNO}_3$  dropwise to effect dissolution. Remove, rinse the cover and sides of the dish, and evaporate just to dryness on a sand bath.

(b) Cool, add 50 ml. of  $\text{H}_2\text{SO}_4$  (1:9), and stir well. Digest and transfer to a 400-ml. beaker, rinsing the dish with 50 ml. of  $\text{HCl}$  (1:1) and a little water. Add 50 ml. of  $\text{HCl}$  (1:1), heat until salts are in solution, cool to  $20^\circ\text{C}$ ., and add a little paper pulp followed by a slight excess of cold, freshly prepared cupferron solution.

(c) Stir well, then filter through a 12.5-cm., medium paper (to which a little paper pulp has been added) into an 800-ml. beaker, and wash 18 to 20 times with cold cupferron wash solution. Discard the precipitate.

(d) To the filtrate add 25 ml. of  $\text{HNO}_3$  and 10 ml. of  $\text{HClO}_4$  (Caution) and evaporate to dense white fumes to ensure complete destruction of all organic matter. Cool, add 150 ml. of  $\text{H}_2\text{O}$ , heat to boiling, and filter through a 9-cm., medium paper into a 400-ml. beaker. Wash the paper 10 times with hot water.

(e) Add 10 g. of  $\text{NH}_4\text{Cl}$ , 5 drops of bromocresol purple, and  $\text{NH}_4\text{OH}$  (1:1), until the color of the solution just changes to purple. Boil for 1 min., allow the precipitate to settle, and filter on an 11-cm., medium paper to which a little paper pulp has been added. Wash 10 times with hot  $\text{NH}_4\text{Cl}$  wash solution. Wash the precipitate and paper pulp back into the beaker, add 100 ml. of  $\text{HCl}$  (1:9) and 10 g. of  $\text{NH}_4\text{Cl}$ , heat to boiling, and repeat the precipitation with  $\text{NH}_4\text{OH}$ , filtering on the same paper and washing as before.

(f) Ignite the precipitate in a platinum crucible, first at a low temperature to burn off the paper, and finally at  $1150^\circ\text{C}$ . to constant weight. Cover the crucible when removing from the furnace, cool in a desiccator, and weigh as soon as possible as  $\text{Al}_2\text{O}_3$  plus  $\text{P}_2\text{O}_5$ .

(g) Fuse the ignited precipitate with 5 g. of  $\text{Na}_2\text{CO}_3$  at  $1100^\circ\text{C}$ . for 30 min. Dissolve the cold melt in 50 ml. of warm water and acidify with  $\text{HNO}_3$ , adding 2 to 3 ml. in excess. Transfer to a 250-ml. Erlenmeyer flask and add 40 ml. of molybdate solution. Complete the determination for phosphorus as described in Paragraphs (e) and (f) of the section on phosphorus by the perchloric acid-alkalimetric method, above. Calculate any phosphorus found to  $\text{P}_2\text{O}_5$  as follows:

$$\text{P} \times 2.295 = \text{P}_2\text{O}_5$$

(h) Calculation.—Calculate the percentage of aluminum as follows:

$$\text{Aluminum, per cent} = \frac{(A - B) \times 0.5291}{C} \times 100$$

where  $A$  = grams of  $\text{Al}_2\text{O}_3$  plus  $\text{P}_2\text{O}_5$ ,

$B$  = grams of  $\text{P}_2\text{O}_5$ , and

$C$  = grams of sample used.

### SILICON BY THE SULFURIC ACID METHOD

*Principle of Method.*—The sample is fused with  $\text{Na}_2\text{O}_2$  in an iron crucible, the melt transferred to a casserole, and acidified with  $\text{H}_2\text{SO}_4$ . The solution is evapo-

## Chapter 26

# ALLOYS: NONFERROUS

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*Scope.*—The classification of alloys as either ferrous or nonferrous is a simplification that originated in days when technology was less complex, and when most metals of construction were either iron-base or copper-base alloys. This major cleavage still identifies the ferrous family rather satisfactorily, as it is restricted to one parent metal; as technology advances, however, it provides less and less individuality for the scores of other alloy families that fall together under the ambiguous, negative side of the classification. But, since the momentum of tradition is with this nomenclature, we must accept our heritage and attempt to define a meaningful area of analytical coverage consistent with the scope of this volume.

The demands of modern technology are so diverse that every metal from lithium to uranium, almost without exception, has been the subject of research for potential usefulness, either as the pure metal or as the base of an alloy system. In the course of this continuing research and development, analytical methods development has kept pace. Some of it is highly specific and specialized within individual research organizations. Some is of great theoretical interest, but as yet, of limited applicability. Obviously, much of this fascinating work is beyond the practical limits of a work devoted to "Industrial Products."

The purpose of this chapter will be to present a series of analytical methods for families of alloys that the analytical chemist is most likely to encounter in general industrial work. This selection includes forty-six methods and covers the following four major nonferrous categories: copper-base alloys; nickel-copper alloys; lead, tin, and antimony alloys; and zinc-base die-casting alloys. Alloy families that have been treated under individual elements in Vol. I are not duplicated, except where a particular method may be required to maintain the continuity of a sequence.

Methods have been chosen with two general objectives in mind: (1) that the chemist consulting this work is interested in a standard or established method that will provide him with an accurate and defensible analysis; or (2) that he is interested in a specification-type analysis, in which good data are required with the greatest possible dispatch. In the methods for copper-base alloys, which doubtless will have the greatest applicability, two sets of methods are provided to meet these two objectives, and assistance in the selection of the appropriate methods is provided.

*Source of Material.*—To enhance the confidence of the chemist in the reliability of these methods, the time-tested methods of the American Society for Testing and

**Hydrochloric Acid.**—It is customary to boil the protein with from 2.5 to 5000 times its weight of 6 *N* HCl under reflux for 18 to 24 hours. When only small amounts of the protein are to be hydrolyzed it is advisable to use 6 *N* HCl equal to 1000 to 5000 times the weight of the protein. This large excess of hydrolyzing acid reduces amino acid losses.

For many purposes, especially for analysis by microbiological methods, 3 *N* HCl at 15 pounds pressure for 5 to 10 hours is also widely employed, but it is not as satisfactory as 6 *N* HCl under reflux when crude proteins are to be analyzed.

It is well recognized that the rate of liberation of some amino acids from peptide linkage is faster than others; furthermore, it is known that the amount of destruction during hydrolysis increases with the length of heating. Thus, for the most accurate work, it is advisable to hydrolyze samples of the protein for different lengths of time, e.g., 20, 40, 80, and 120 hours, and to determine the amino acid composition of each hydrolyzate. Then if it is observed that one or more amino acids (e.g., cystine, methionine, serine, threonine) show a progressive decrease, the true value may be assumed to be that found at zero time from a plot of the values obtained at different periods of hydrolysis. Likewise, if the quantity of an amino acid (e.g., isoleucine, valine) gradually rises to a peak value, the assumed maximal value may be obtained graphically. These refinements are only valuable when the methods employed have the highest accuracy, and must be applied empirically for each separate protein. When investigating highly purified proteins it is also advisable to redistill the HCl several times in glass.

Chromatographic assay methods require complete hydrolysis to amino acids for obvious reasons. Complete hydrolysis is also necessary when microbiological assay methods are employed, because the growth response of many organisms is different (it may be greater or less) for the free amino acid than for the same amino acid in peptide linkage.

A point too often forgotten in many laboratories is that destruction of amino acids can take place even after the hydrolysis is ended, especially when the hydrolyzate contains free acid and humin. It is advisable, therefore, to remove the excess HCl as soon as possible after hydrolysis, filter off the humin, decolorize with a small quantity of charcoal (Darco G-60), if necessary, and after evaporation to dryness, dissolve the amino acid hydrochlorides in 10% vol./vol. 2-propanol and store in the cold.

**Sulfuric Acid.**—Although 8 *N* H<sub>2</sub>SO<sub>4</sub> at atmospheric pressure is usually employed, other concentrations of acid and pressures may be used.<sup>4</sup> The advantage of H<sub>2</sub>SO<sub>4</sub> lies in the ease with which the excess acid can be removed with Ba(OH)<sub>2</sub>. The humin is also largely precipitated along with the BaSO<sub>4</sub>. H<sub>2</sub>SO<sub>4</sub> is less effective, at equal concentrations, than HCl.

NOTE.—Other methods of hydrolysis are given in Block and Weiss (1956).<sup>1</sup>

### USE OF BASES

Sodium hydroxide, 5 *N*, or 14% wt./vol. barium hydroxide under reflux for 18 to 20 hours must be employed for liberating *tryptophan* from the protein. The excess barium ions are removed by neutralizing the diluted hydrolyzate with gaseous or solid CO<sub>2</sub> (Dry Ice).

<sup>4</sup> Block, R. J., in Alexander, P., and Block, R. J., *Analytical Methods of Protein Chemistry*, Vol. 2, Pergamon Press, London, 1961.

## USE OF ENZYMES

Proteolytic enzymes are usually not practical for the preparation of hydrolyzates for chromatographic methods and not advised for microbiological procedures<sup>2</sup> because they contribute some amino acids to the final solution.

However, if enzymatic hydrolysis is desired (enzymatic hydrolysis is required for the liberation of iodoamino acids from iodoproteins), it is advisable to first denature the protein by heat coagulation at pH 4 (dilute acetic acid) and then to digest at 40°C. at pH 8.6 in 0.01 *M* borate buffer for at least 24 hours with one-tenth the weight of the protein of pancreatin powder (Viokase, Viobin Corporation, Monticello, Ill.); the enzyme is then inactivated by boiling and removed by filtration. After cooling the solution, the resulting peptides are hydrolyzed with an amount of erepsin equal in weight to the pancreatin.

## COMPLETENESS OF HYDROLYSIS

The liberation of carboxyl and amino groups from peptide linkage is the object of protein hydrolysis. Hydrolysis is considered complete when a maximum number of  $-\text{COOH}$  and  $-\text{NH}_2$  groups have been liberated. The carboxyl groups can be readily estimated by one of the modifications of the Schill-Sørensen formal titration method or by oxidation with ninhydrin.

## REACTION OF AMINO ACIDS WITH NINHYDRIN

Ammonia resulting from the oxidative deamination of amino acids with ninhydrin is aerated or steam distilled<sup>5</sup> into boric acid and titrated.<sup>7</sup>

*Reagents.* Caprylic Alcohol.—Saturate with thymol.

Ninhydrin (Solid).

Citrate Buffer, pH 2.5.—Grind 2.06 g. of trisodium citrate and 19.15 g. of citric acid to a fine powder.

Hydrogen Peroxide, 30%.

Potassium Hydroxide, Saturated.—To a cylinder containing water under mineral oil 1-inch thick, add solid KOH to saturation. Preserve under oil.

Indicator.—Add 10 parts of 0.1% bromocresol green to 1 or 2 parts of 0.1% methyl red in 95% ethanol.

Boric Acid.—Dilute 20 g. of  $\text{H}_3\text{BO}_3$  to 1 liter. Add 20 ml. of indicator per liter.

Hydrochloric Acid.—Standard 0.0714 *N* HCl.

*Procedure.*—Add 1 ml. of solution containing 20 to 100  $\mu\text{g.}$  of carboxyl nitrogen to an aeration tube containing 0.3 mg. of buffer and 50 mg. of ninhydrin. The pH should be 2.4 to 2.6. Shake to mix and place in boiling water for 10 minutes. At the end of 2 minutes of heating, shake to dissolve the ninhydrin. After 10 minutes of heating, add 3 drops of 30%  $\text{H}_2\text{O}_2$ , shake, and heat for 3 minutes longer. Set up the tubes for aeration or distillation. Add 1 ml. of saturated KOH and aerate into  $\text{H}_3\text{BO}_3$  for 40 minutes using 1.5 ml. of 2% boric acid to trap the ammonia. Titrate<sup>8</sup> with HCl or  $\text{KHIO}_3$ . Calculate as follows:

$$\text{Ml. of } 0.0714 \text{ } N \text{ HCl} \times 1000 = \text{mg. of amino acid } N$$

<sup>5</sup> Block, R. J. and Bolling, D., *The Amino Acids Composition of Proteins and Foods*, 2nd Ed., Charles C Thomas, Publisher, Springfield, Ill., 1951.

<sup>6</sup> The Conway Microdiffusion Method may also be used. See McConnell, W. B., *Can. J. Chem.*, 30, 522-528, 1952.

<sup>7</sup> Sobel, A. E., Hirschman, A., and Besman, L., *J. Biol. Chem.*, 161, 99-103, 1945.

<sup>8</sup> The quantity of ammonia may be also estimated colorimetrically. See Brown, R. H., Duda, G. D., Korkes, S., and Handler, P., *Arch. Biochem. Biophys.*, 66, 301-309, 1957.

## COLORIMETRIC ESTIMATION OF AMINO GROUPS

**Harding and MacLean's<sup>9</sup> (1916) Method.**—To 1 ml. of neutralized unknown (0.01 to 0.08 mg. of amino nitrogen) add 1 ml. of 10% aqueous pyridine and 1 ml. of 2% aqueous ninhydrin. Stopper the test tube lightly with a cotton plug and place in a boiling water bath for 20 minutes. Cool in water, dilute to 50 ml. and read at 570  $m\mu$ . Leucine may be used to prepare the standard curve.

**Yemm and Cocking's Method.<sup>10</sup>**—Mix 1 ml. of an amino acid solution containing 0.05 to 2.8  $\mu$ g. amino nitrogen with 0.5 ml. citrate buffer of pH 5 (0.2 M). Add ninhydrin in methyl Cellosolve (0.02 ml., 5% wt./vol.) and KCN in methyl Cellosolve (1 ml., 2% wt./vol.) to this solution either separately or as a single solution. Separately these reagents are stable for at least one month, and mixed, for at least one week. Heat the well-mixed solution for at least 15 minutes at 100°C. and cool for 5 minutes in running tap water. The boiling point of the water-methyl Cellosolve mixture is greater than 100°C., and using tubes stoppered with a glass marble, evaporation losses during the heating period are negligible. Make the solution up to a convenient volume with ethanol (60% wt./vol.) and determine the optical density at 570  $m\mu$ . The colors are quite stable for at least 1 hour at room temperature. Most of the common amino acids give colors equivalent to  $100 \pm 1\%$  of that of pure dioxohydrindylidene-dioxohydrindamine (DYDA) except tryptophan (80%) and lysine (110%). Ammonia reacts yielding a color equivalent to only 33% of that of pure DYDA.

## QUALITATIVE PAPER CHROMATOGRAPHY

Present-day paper chromatography may be considered to have started with the report of Martin and Synge<sup>11</sup> in 1941. Because of the extensive familiarity with this method and its adequate coverage in many books and review papers<sup>12</sup> a description of only a few useful procedures will be given.

**Quantities of Amino Acids Used.**—The amount of each amino acid required to give a visible spot on a two-dimensional chromatogram is dependent on: type of color reagent, size of spot initially applied, length of development, type of paper, solvents employed, and the nature of the amino acid. The approximate amounts in 5  $\mu$ l. of solution of each amino acid to be applied to a large (18 in. x 22 in.) two-dimensional chromatogram are given in Table 27-1.

**Reagents and Materials.** Paper.—Whatman No. 1 or No. 3 or Schleicher and Schuell No. 598 is most widely used. The latter is especially valuable for cystine, methionine, histidine, and tyrosine when one-dimensional chromatography and specific color tests are employed.

**Solvents.<sup>13</sup> Phenol.**—One-hundred milliliters of metal-free water are dissolved in 500 ml. of Mallinckrodt Gilt Label liquid phenol by gentle warming. Add 25 to 50 mg. of 8-hydroxyquinoline. The solvent is stored in a dark bottle in the

<sup>9</sup> Harding, V. J., and MacLean, R. M., *J. Biol. Chem.*, **24**, 503-517, 1916.

<sup>10</sup> Yemm, E. W., and Cocking, E. C., *Analyst*, **80**, 209-213, 1955.

<sup>11</sup> Martin, A. J. P., and Synge, R. L. M., *Advances in Protein Chem.*, **2**, 1-83, 1945.

<sup>12</sup> Block, R. J., Durrum, E. L., and Zweig, G., *Paper Chromatography and Paper Electrophoresis*, 2nd. Ed., Academic Press, Inc., New York, 1958.

<sup>13</sup> The addition of a drop of 0.1% wt./vol. bromocresol purple indicator to the amino acid solution is often helpful in enabling the investigator to follow the length of the solvent development, especially if the solvent is allowed to flow off the paper.

TABLE 27-1. DESIRABLE QUANTITIES OF EACH AMINO ACID TO BE APPLIED TO A TWO-DIMENSIONAL CHROMATOGRAM IN 5  $\mu$ l. OF SOLUTION

Arg..... 4 $\mu$ g.	Tyr.... 4 $\mu$ g.	Cys..... 5 $\mu$ g.	Ser..... 1 $\mu$ g.
His..... 10 $\mu$ g.	Try.... 4 $\mu$ g.	Cysteic ac..... 1 $\mu$ g.	The..... 1 $\mu$ g.
Lys..... 3 $\mu$ g.	Phe.... 4 $\mu$ g.	Met..... 2 $\mu$ g.	Pro..... 3 $\mu$ g.
Leu..... 1 $\mu$ g.	Glu.... 0.5 $\mu$ g.	Gly..... 0.5 $\mu$ g.	Hop..... 3 $\mu$ g.
Iso..... 1 $\mu$ g.	Asp.... 1 $\mu$ g.	Ala..... 0.5 $\mu$ g.	
Val..... 1 $\mu$ g.			

refrigerator where the cold causes separation into two layers. When it is to be used, the bottle is vigorously shaken and the desired quantity of the emulsion is removed and gently warmed to effect solution.

A beaker containing 100 mg. of NaCN in 4 to 6 ml. of water and one containing 50 ml. of 3 to 4%  $\text{NH}_3$  are commonly placed in the chamber.

The relative distance ( $R_f$ ) traveled by the more basic amino acids (arginine, lysine, ornithine, hydroxylysine) in phenol is influenced by the pH of the developing medium. Thus, if a beaker containing 3%  $\text{NH}_3$  is placed in the chamber, these amino acids will travel further in the solvent than in its absence.

*1-Butanol:Acetic Acid.*—1-Butanol:glacial acetic acid:water = 150:50:125 vol./vol.

*2-Butanol:Ammonia.*—2-Butanol:3% aqueous  $\text{NH}_3$  = 150:50 vol./vol. Three per cent aqueous ammonia is prepared by diluting 55 ml. of concentrated  $\text{NH}_4\text{OH}$  to 500 ml. with water.

*2-Butanol:Ammonia.*—2-Butanol:concentrated  $\text{NH}_4\text{OH}$  = 150:50 vol./vol. Run the chromatogram in an atmosphere of concentrated  $\text{NH}_4\text{OH}$ .

*tert-Butyl Alcohol:Formic Acid.*—*tert*-Butyl alcohol:88% formic acid:water = 70:15:15 vol./vol.

**Apparatus.** Descending Chromatography.—In this technique the solvent is permitted to flow along the paper in a *downward* direction. Consden, Gordon, and Martin<sup>14</sup> first reported the successful separation of a mixture of amino acids by descending paper chromatography.

The essentials of the apparatus consists of a filter paper strip, the upper end of which is immersed in a glass trough containing the solvent. The strip is hung in an airtight chamber. After the insertion of the paper, the chamber is sealed with Saran wrap and glass plate. The bottom of the chamber is covered with the organic solvent in order to provide a saturated atmosphere. The trough is provided with a glass bar which serves as the paper support, and the paper strip is passed over a glass rod to prevent capillary siphoning of the solvent down the paper.

**Ascending Chromatography.**—Ascending paper chromatography is especially suitable for quick analyses of a large number of samples or for exploratory work involving the use of many different solvents. One must bear in mind, however, that the upward flow of solvent is eventually counteracted by gravity, resulting in a definite slow-up after the solvent front has traveled more than 25 cm. The chromatographic development should be stopped at this point. In order to achieve

<sup>14</sup> Consden, R., Gordon, A. H., and Martin, A. J. P., *Biochem. J.*, 38, 224-232, 1944.



maximum resolution by this method, "multiple development" should be tried (see below). Suitable equipment for ascending chromatography is described below.

**Ascending-Descending Chromatography.**—Rectangular glass aquaria, 52 cm. long, 32 cm. and 26 cm. wide, are used. The lower portion of the sides and all the joints are covered by a layer of paraffin. Two glass rods running the width of the chamber are sealed with paraffin to the sides of the chamber about 1 cm. out and 4 cm. from the top. These rods support lengthwise rods on which the paper is placed. If ascending chromatography is used, short sheets of paper are held between two rods clamped by rubber bands. Glass or stainless steel troughs are used. The chamber is covered with *Saran* wrap and a glass plate.

**Two-Dimensional Chromatography.**—For maximum resolution of a complex mixture, two-dimensional paper chromatography is recommended. The principle of this technique is the successive development of the chromatogram with two different solvents (e.g., a basic and an acidic solvent), the advancing fronts of which are at right angles to each other.

The same apparatus as described for unidimensional chromatography, or the smaller equipment described by Datta *et al.*,<sup>15</sup> will lend itself to two dimensional chromatography with the difference that a single spot is applied 2.5 cm. from the lower corner of a sheet. After the first solvent has traveled almost to the top edge, the sheet is removed, dried, and rerun in a second solvent which is at right angles to that of the first solvent. If decomposition products accumulate at or near the solvent front of the first solvent, it is advisable to cut off this section of the paper.

**Multiple Development.**—Multiple development technique is used to gain a greater effective distance of solvent front while retaining a shorter length for the paper itself. After the mixture has been separated by the solvent and the paper dried, it is returned to the solvent trough for a repetition of the passage of solvent. This process may be repeated 2 to 4 times.

It is sometimes desirable to use a "fast" solvent to get rid of unwanted substances or impurities. These may then be located by suitable detection methods and the paper sheet cut off parallel to the solvent flow just below this region. The remaining part of the sheet is fastened with a sewing machine to another piece of filter paper of the same width, and a second development (with the same or another solvent) is undertaken.

**Circular or Horizontal Filter-Paper Chromatography.**—The principle of this technique is that the substances to be analyzed are resolved into circular zones instead of spots. A "tail" is cut from a circular filter-paper disk and is immersed into the developing solvent after the substances to be analyzed have been deposited in a circle on the paper on a radius of 1 cm. from the center and 1 to 2 cm. apart.

The apparatus consists of two upper or lower sections of a Petri dish and a filter-paper disk slightly larger than the glass sections. The "tail" is fashioned by making two parallel cuts, about 2 mm. apart, from the same edge up to the center of a circular filter paper, and the tail is bent at the joint perpendicular to the plane of the paper and cut down to about 1.5 cm. in length. Care must be taken that the cuts are of equal length; otherwise the development may not result in truly circular zones.

Instead of fashioning the wick from the filter-paper disk itself, it may be formed from another strip of filter paper (0.5 x 1.5 cm.), which is folded in the center and inserted into a 0.5-cm. long slit in the center of the filter-paper disk. The wick

<sup>15</sup> Datta, S. P., Dent, C. E., and Harris, H., *Science*, 112, 621-623, 1950.

may also be made from a strip of filter paper, rolled into a cylinder (2 to 3 mm. thick), cut at the end into the form of a brush and inserted through a small hole at the center of the disk or the solvent may be fed onto the paper disk by means of a glass capillary. The size of the capillary regulates the rate of feed and thus the rate of development. A small cone made of filter paper and placed with its apex at the center of the disk may also be used as an irrigating wick.<sup>12</sup>

*Application of Sample (Spotting).*—Probably the most important single factor for successful paper chromatography is the proper application of the sample onto the filter paper. The original spot must be small (5 mm. in diameter), and for quantitative work the spot size and the deposited volume must be absolutely uniform.

Self-filling micropipets are available in sizes ranging from 1 to 10  $\mu$ l. (1  $\mu$ l. = 0.001 ml.). The tip is immersed in the solution to be chromatographed and filled to the mark by capillarity. The tip is then lightly touched to the mark on the paper onto which it empties with an even flow. In order to keep the spot size to a minimum diameter, the solution may be dried as it flows on the paper either with an infrared lamp or a hair drier. The filter paper may rest on a clean glass or plastic plate. There is very little loss of material, because any solution which reaches the glass is immediately reabsorbed on the underside of the paper. The pipets are cleaned with hot soapy water, distilled water, and acetone, in this sequence.

In ascending chromatography, the spots are usually placed about 2 to 3 cm. from the lower edge of the paper, 2 to 2.5 cm. apart from each other. The positions are indicated by pencil marks. A simple device for making a large number of sheets is as follows: A strip of sheet aluminum is marked with raised points, 2 or 2.5 cm. apart, with the point of a nail. The lower edge ( $\frac{1}{4}$  in.) is bent slightly back to form a small ledge. The chromatogram is then placed between two sheets of filter paper and fitted into the aluminum template. A quick movement of the thumb across the protective paper will thus mark the chromatogram conveniently.

When more than one chromatogram is run simultaneously, the filter papers are placed on clean glass plates, one over the other in echelon, each separated by a glass plate. It is important to hold the papers flat on the glass plates. This is accomplished by placing the covering plate about 1 cm. above the point where the spot will be applied. Spotting platforms made from wood with removable glass plates (1 in. wide) and flush with the surface of the platform have also been used. This technique is more convenient than the former, because between runs only the thin glass plates instead of the larger plates of glass have to be cleaned.

For best results not more than 5  $\mu$ l. of solution should be applied at one time. If more than this quantity is desired, other aliquots are applied on top of the initial spot. The spots are dried after each application with an infrared lamp or the warm air blast from a hair drier. If the applied spot is too large initially, the shape of the spots on the developed chromatogram becomes diffuse and indefinite.

When applying as much as 25 to 50  $\mu$ l. of a solution, it is recommended to use transfer-type pipets. The flow of liquid from this pipet is controlled with a micro syringe equipped with a screw control.

Other methods are described in Block, Durrum, and Zweig.<sup>12</sup>

*Effect of Chamber Size.*—The chamber size affects the  $R_f$  values of amino acids.<sup>13</sup> A critical solvent volume has been found which is dependent on the size of the

<sup>13</sup> Clayton, R. A., Anal. Chem., 28, 904-906, 1956.

chromatographic cabinet. For example, a 37-l. cabinet has a critical solvent volume of 375 ml. Above the critical solvent volume the  $R_f$  values are at a minimum, even when the solvent volume is increased. Below the critical solvent volume the  $R_f$  values are at a maximum. It is, therefore, recommended to stay above the critical solvent volume for constant  $R_f$  values. It appears that below the maximum critical solvent volume unequal vaporization occurs, the solvent becomes richer in water, and, hence, the  $R_f$  values of the water-soluble amino acids tend to increase.

**Drying the Chromatogram.**—The chromatogram should be dried thoroughly to remove any excess solvent prior to color development. When phenol is used as a solvent, the chromatogram is dried at room temperature in order to prevent decomposition of some amino acids. Drying the chromatograms at elevated temperatures may be accomplished in a hood with the aid of a fan-type electric heater.

**Color Development.**—A choice of color reactions is given below for each class of amino acids.

**Dipping.**—Dipping of the chromatograms is recommended. It is necessary, of course, to choose a solvent for the color reagent in which the substances to be detected are insoluble. A tray for dipping chromatograms consists of one of the chromatogram troughs, and a tube weighted with lead shot. The dried chromatogram is slipped under the roller tube and is drawn quickly through the reagent solution.

A multiple dipping procedure for the amino acids utilizes three to four successive color reagents: ninhydrin or isatin, Ehrlich reagent (dimethylaminobenzaldehyde), Sakaguchi, or diazo reagents.<sup>11</sup> The spots should be marked in pencil after each reagent. In this manner most of the amino acids may be identified on the same chromatogram by their position and characteristic color reactions.

**Spraying.**—For the spraying of chromatograms, a glass atomizer may be made with only moderate skill in glass blowing.<sup>12</sup> De Vilbiss atomizers are satisfactory if the spray solution is not metal-corrosive. Commercial all-glass spray bottles of various sizes are available. A ninhydrin-aerosol spray for amino acid chromatograms has also been developed. This atomizer does not require a source of compressed air and may be useful for portable applications.<sup>13</sup>

Chromatograms are sprayed in a chemical hood by hanging the papers on a suitable rack by means of clothespins. The atomizer is held at a distance 12 to 15 in. from the paper and is moved in a slow, but even, left to right movement, starting at the top of the paper and working downward. Care must be exercised not to overload the paper with spraying reagent, because the spots tend to diffuse and migrate, especially when aqueous reagents are employed.

The spots of a chromatogram may also be detected by laying the dried chromatogram on a wet sheet soaked with the color reagent.<sup>13</sup>

**Ninhydrin Test. Method 1.**—Ninhydrin, 0.25% wt./vol., in acetone containing 5% wt./vol. pyridine, lutedine, or collidine. Warm at 35°C. for 1 hour in a moist chamber, store in the dark overnight.

**Method 2.**—Ninhydrin, 0.3%, in 95% ethanol. The color is developed at room temperature in the dark for 18 hours.

**Method 3.**—Two grams of ninhydrin are dissolved by warming in 50 ml. of water. To this solution, 80 mg. of stannous chloride in 50 ml. of water are added. The

<sup>11</sup> Jepson, J. B., and Smith, I., *Nature*, 172, 1100-1101, 1953.

<sup>12</sup> Zweig, G., *Anal. Chem.*, 28, 428, 1956.

<sup>13</sup> Bowden, C. H., MacLagan, N. F., and Wilkinson, J. H., *Biochem. J.*, 59, 93-97, 1955.

mixture is allowed to stand in the dark for 24 hours or longer, after which the precipitate is removed by filtration. This stock solution of 2% ninhydrin will remain useful for many months if kept in the refrigerator. Twenty-five ml. of stock ninhydrin solution are diluted to 50 ml. with water; then 450 ml. of isopropanol are added.

*Method 4.*—When alkaline salts have been used to buffer the paper or where the material to be chromatographed contains a considerable quantity of alkali, the alkali must be neutralized by the incorporation of 2 to 4% vol./vol. of acetic acid into the ninhydrin solution.

**Conservation of Amino Acid Chromatograms Stained with Ninhydrin.**—The ninhydrin-treated chromatogram is dipped into dilute copper nitrate (1 ml. of saturated aqueous  $\text{Cu}(\text{NO}_3)_2 + 0.2$  ml. of 10% vol./vol.  $\text{HNO}_3$  are diluted to 100 ml. with ethanol). The papers are quickly neutralized with  $\text{NH}_3$  vapors, air dried and sprayed with Krylon crystal clear acrylic spray (Krylon, Inc., Philadelphia 40, Pa.).<sup>12</sup>

## SPECIFIC REAGENTS FOR THE AMINO ACIDS

### ARGININE

**1-Naphthol-Hypochlorite Reagent (Sakaguchi Reaction).**—The chromatograms are sprayed with 0.1% solution of 1-naphthol in 1 *N* NaOH. After drying, the paper is sprayed with NaClO solution prepared from an equal mixture of ethanol and commercial NaClO (Clorox). Arginine appears as a red spot; 10  $\mu\text{g}$ . or more must be used.

Dissolve 0.01% 1-naphthol in ethanol containing 5% urea. Add KOH to 5% wt./vol. just before spraying. Spray and air dry a few minutes, and spray lightly with 0.7 ml. of  $\text{Br}_2$  in 100 ml. of 5% wt./vol. KOH. This test is sensitive to 0.2  $\mu\text{g}$ . of arginine.

**8-Hydroxyquinoline.**—A modified Sakaguchi method consists in dipping the chromatogram into 0.1% 8-hydroxyquinoline in acetone. After the chromatogram has dried, it is dipped into a solution of 0.02 ml. of  $\text{Br}_2$  in 100 ml. of 0.5 *N* NaOH. Arginine and other guanido compounds give orange-red spots.

**Ferricyanide-Nitroprusside Reagent.**—Mix 1 volume of 10% wt./vol.  $\text{K}_3\text{Fe}(\text{CN})_6$ , 1 volume of 10% wt./vol.  $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$  and 1 volume of 10% wt./vol. NaOH. After 30 minutes add 9 volumes of water and 12 volumes of acetone.

### CYSTINE<sup>20</sup> (cf. Methionine)

**Phospho-18-Tungstic Acid.**—The paper is dipped into 1% wt./vol. of  $\text{Na}_2\text{SO}_3$  and partly dried in air. Then the damp chromatogram is treated with Folin's phospho-18-tungstic acid reagent made alkaline with  $\text{NaHCO}_3$ . Cysteine and other reducing substances give a deep-blue color without sulfite treatment (cf. Histidine, Egothionine, etc.).

**Cysteine and Homocysteine.**—The hydrolyzate containing these sulfhydryl compounds is adjusted to pH 5 and treated with an excess of HCHO for 24 hours at room temperature.

**Feigl's Sodium Azide-Iodine Reaction.**—The dry chromatograms are sprayed with 0.05 *N* iodine in 50% ethanol containing 1.5% wt./vol. of sodium azide or

<sup>20</sup> Toennies and Kolb have shown that cysteine is oxidized after application to the filter paper in several days. The various oxidation products were separated with phenol:2-propanol: $\text{H}_2\text{O}$  = 80:15:15 vol./vol. See Toennies, G., and Kolb, J. J., *Nature*, 177, 281-282, 1956.

a freshly prepared solution of 0.01 M  $I_2$  in 0.5 M KI plus 0.5 M  $NaN_3$  vol./vol. The sensitivity of this reagent is 0.5  $\mu$ g. of methionine.

**Sodium Nitroprusside.** *Reagent 1:*—Sodium nitroprusside (1.5 g.) is dissolved in 5 ml. of 2 N  $H_2SO_4$ . Then 95 ml. of methanol and 10 ml. of 28% wt./vol. ammonia are added. The solution is filtered and stored in the refrigerator. *Reagent 2:* Two grams of NaCN are dissolved in 5 ml. of water and diluted to 100 ml. with methanol. *Tests:* For cysteine, use reagent 1; for cystine dip into reagent 1, dry slightly, and, while still damp, dip into reagent 2; for both cysteine and cystine, prepare reagents at double strength and treat with an equal mixture of 1 and 2.

**Platinic Iodide.**—Add in the following order 1 ml. of 0.002 M  $H_2PtCl_6$ , 0.25 ml. of 1 N KI, 0.4 ml. of 2 N HCl, and 38 ml. of acetone. (The acetone must be purified by refluxing over and distillation from  $KMnO_4$  and  $K_2CO_3$ .) The dried chromatograms are dipped into this reagent. Cystine, cysteine, methionine, and some other reducing substances give a white spot on a red-purple background.

The reagent may be used after development with butanol-acetic acid and other alcoholic solvents without extra precautions. If phenol, lutidine, etc., are the developing solvents, all traces must be removed with ether-acetone (vol./vol.), petroleum ether, etc. Palladous chloride in 0.1 N HCl may be used in place of chloroplatinic acid.

**N-Ethylmaleimide.** The air-dried chromatogram is dipped into 0.05 M N-ethylmaleimidenem in absolute 2-propanol. After drying in air the color is developed by dipping the chromatogram into 0.25 M KOH in 2-propanol.<sup>21</sup> Compounds which contain -SH groups give pink to red spots.

**Oxidation and Coupling of Sulfur Amino Acids.**—Cystine may be converted to cysteic acid, and methionine into methionine sulfoxide and sulfone, by oxidation with  $H_2O_2$ . The sample is applied to the paper, and the spot is dried. Then an aliquot (equal to that of the amino acid solution) of 30% wt./vol. of  $H_2O_2$  followed by two or three times that quantity of 0.02% wt./vol. of ammonium molybdate is applied in the usual manner. Cysteic acid, methionine sulfoxide, and methionine sulfone are more readily identified on phenol-lutidine two-dimensional chromatograms than are the parent amino acids.

In order to avoid destruction of cysteine, reduced glutathione, etc., on paper chromatograms, the -SH compounds are coupled with *n*-ethylmaleimide by dissolving the neutralized mixture of amino acids in aqueous 0.1333 . . . M reagent. It is important to keep the pH of the NEM-derivatives at pH 7 or below during the entire operation. The NEM-adducts readily decompose above pH 7.5. The S-substituted compounds may then be determined by the ninhydrin reaction, treatment with 0.25 M KOH in 2-propanol or by the use of some of the sulfur tests.

### HISTIDINE

**Sulfanilamide.**—Place 5 ml. of sulfanilamide and 5 ml. of  $NaNO_2$  in a separatory funnel. Mix for 1 minute. Then add 50 ml. of 1-butanol. Shake for 1 minute, and let stand for 4 minutes. Decant the butanol layer, and spray or dip the chromatogram. Dry the sheet in a current of air and then spray with half-saturated  $Na_2CO_3$ . Imidazoles give a deep cherry-red color.

***p*-Anisidine.**—Mix equal volumes of 1% wt./vol. *p*-anisidine in 0.11 N HCl and 10% wt./vol. amyl nitrite in ethanol. Let stand 3 to 5 minutes and spray paper.

<sup>21</sup> Benesch, R., Benesch, R. E., Gutcho, M., and Laufer, L., *Science*, 123, 981-982, 1956.

Dry the sheets at room temperature, and develop the color either with  $\text{NH}_3$  vapors or by spraying with 10% KOH in ethanol.

*p*-Bromaniline.—The reagent may be substituted for sulfanilamide. It is especially valuable for histidine and other imidazoles as it gives a relatively weak reaction with tyrosine and other phenolic derivatives.

### GLYCINE

Glycine, as well as histidine and tryptophan, gives a color when sprayed with *o*-phthalaldehyde 0.2% wt./vol. in acetone.

### METHIONINE ["Active Methionine" and other Sulfur Compounds (Thiohydantoins)]

Platinic Iodide.—See Cystine, above.

Sodium Nitroprusside.—Dissolve 500 mg. of sodium nitroprusside in 10 ml. of water at room temperature. Then add 500 mg. of  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , followed by 1 g. of  $\text{NaHCO}_3$ . After the evolution of gas has stopped, add two drops of  $\text{Br}_2$ . Remove the excess  $\text{Br}_2$  by aeration, filter the dark-green or black-brown solution, and dilute to 25 ml. It is stable for 2 weeks. Let stand 24 hours, filter again, and store in the dark. Just before use, dilute the reagent with an equal volume of saturated  $\text{Na}_2\text{CO}_3$ , and filter. Spray, and expose moist chromatograms to steam for a few minutes.

### ORNITHINE

Vanillin.—Spray with a freshly prepared solution of 2% vol./vol. vanillin in 1-propanol. Heat at  $110^\circ\text{C}$ . for 10 minutes, then spray with 1% wt./vol. KOH. Heat at  $110^\circ\text{C}$ . for 10 minutes. Five-tenths microgram of ornithine gives a yellow-brown color; sarcosine gives red spots. The procedure may be modified as follows: Spray with 0.2% vol./vol. vanillin in acetone followed by 1% wt./vol. alcoholic KOH. Heat. Ornithine, proline, and hydroxyproline give red spots.<sup>22</sup>

### PROLINE AND HYDROXYPROLINE

Isatin.—Spray with 0.2% wt./vol. isatin in acetone. Heat for 10 minutes in  $\text{H}_2\text{O}$ -saturated oven at  $70^\circ$  to  $75^\circ\text{C}$ . Proline and hydroxyproline give blue colors; cystine and tyrosine often also give blue colors. Glutamic and aspartic acids give pink spots which turn blue on standing. The other amino acids give pink spots which fade.

The air-dried chromatograms are heated 2 to 3 minutes at  $110^\circ\text{C}$ ., then they are dipped into 0.4% wt./vol. isatin in butanol:acetic acid = 96:4 vol./vol. After drying in air, the paper is heated for 10 to 15 minutes at  $110^\circ\text{C}$ ., it is then dipped into *N* HCl and, while still damp, the excess HCl is washed out with distilled water. Only the proline spot remains.<sup>23</sup>

Isatin-*p*-Dimethylaminobenzaldehyde.—After heating the isatin-treated paper, it is sprayed with a freshly prepared solution of 1 g. of *p*-dimethylaminobenzaldehyde, 90 ml. of acetone, and 10 ml. of concentrated HCl. Only hydroxyproline will give a purple-red color.<sup>17</sup> Sensitivity, 0.1  $\mu\text{g./cm.}^2$

<sup>22</sup> Curzon, G., and Giltrow, J., *Nature*, 173, 314-315, 1954.

<sup>23</sup> Pasiecka, A. E., and Morgan, J. F., *Proc. Soc. Exptl. Biol. Med.*, 93, 54-57, 1956.

## SERINE AND THREONINE

Spray with 0.035 *M* periodic acid in methanol containing 2% vol./vol. distilled  $\gamma$ -collidine and air dry. Serine, hydroxylysine, etc., are revealed by dipping the oxidized chromatogram into a mixture of 15 g. of  $\text{CH}_3\text{COONH}_4$ , 0.3 ml. of  $\text{CH}_3\text{COOH}$ , and 1 ml. of acetylacetone per 100 ml. of methanol. Air dry, and view under ultraviolet light.

Threonine is revealed by spraying with a freshly prepared mixture of 5% wt./vol. methanolic  $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ :20% vol./vol. methanolic piperidine = 1:1 vol./vol.<sup>24</sup>

## TAURINE

*o*-Phthaldialdehyde.—Dip the chromatogram in 0.2% wt./vol. *o*-phthaldialdehyde plus 0.2% wt./vol. urea in acetone. Heat for 10 minutes at 50°C. Dip into 1% wt./vol. alcoholic KOH; heat for 10 minutes at 50°C. and for 10 minutes at 105°C. Taurine gives a red spot.<sup>22</sup>

## TRYPTOPHAN

Ehrlich's Reagent.—Prepare fresh a mixture of 1 g. of *p*-dimethylaminobenzaldehyde, 90 ml. of acetone, and 10 ml. of concentrated HCl. The Ehrlich reaction may be stabilized by first spraying the chromatogram with 1% wt./vol. methionine, drying in air, and then spraying with *p*-dimethylaminobenzaldehyde in HCl-acetone.<sup>23</sup>

## TYROSINE (Diiodotyrosine, Thyroxine, etc.)

Pauly Reagents.—These are described above (Histidine).

Ceric Sulfate—Sodium Arsenite—Methylene Blue Reaction for Iodoamino Acids.—Reagents: A.  $\text{Ce}(\text{HSO}_4)_4$ :10% wt./vol. in 10%  $\text{H}_2\text{SO}_4$  vol./vol. B.  $\text{NaAsO}_2$ , 5% wt./vol. in  $\text{H}_2\text{O}$ . C. Methylene blue, 0.05% wt./vol. in  $\text{H}_2\text{O}$ . All reagents must be made up in deionized-distilled  $\text{H}_2\text{O}$ .

The chromatogram is lightly sprayed on both sides with a freshly prepared mixture of A and B in the proportion of 2:3 vol./vol. An 18½ x 22½ in. sheet of Whatman No. 3 paper requires about 50 ml. of the reagent. The paper is dried in an air stream for 5 minutes. It is then sprayed on both sides with reagent C approximately 100 ml. per sheet. The sheet is again dried for 5 minutes. It is then placed in a tank containing  $\text{NH}_3$  vapors until the  $\text{H}_2\text{SO}_4$  has been neutralized. This is indicated by the change in color of the background from pink to yellow. The chromatogram is then dried in air. The iodoamino acids appear as bright-blue spots on a yellow-green background.

DIFFERENTIATION OF  $\alpha$ -AMINO ACIDS  
FROM OTHER AMINO COMPOUNDS

The dried chromatograms are dipped into a methanolic solution of 0.25% wt./vol. cupric nitrate and 2% wt./vol. sodium acetate. The paper is dried at 70°C. for 2 minutes and then counterstained with 0.2% wt./vol. ninhydrin in acetone.  $\alpha$ -Amino acids are not colored or only very faintly after drying in air for 1 minute followed by heating at 70°C. for 40 to 50 seconds. Other ninhydrin positive com-

<sup>24</sup> Schwartz, D. P., Anal. Chem., 30, 1855-56, 1958.

<sup>23</sup> Nakajima, S., and Okuyama, G., J. Pharm. Soc. Japan, 76, 620-624, 1956.

pounds including lysine give intense purple colors. Glycine and glycine-containing peptides are yellow or orange.

Another procedure for differentiating  $\alpha$ -amino acids from  $\beta$ -amino acids, amines, etc., is based on the nonenzymatic transamination of the former.<sup>26</sup> The paper chromatogram is sprayed with alcoholic pyridoxine, or Vitamin B<sub>6</sub> (250 mg. of Vitamin B<sub>6</sub>·HCl in 100 ml. of 95% ethanol neutralized to pH 5.5) and air dried. The chromatogram is heated at 90°C. for 10 minutes to effect transamination and then sprayed with ninhydrin to reveal unreacted amino acids and primary amines.

### DETECTION OF OPTICAL ISOMERS OF AMINO ACIDS

The presence of a D-isomer can often be detected by spraying a paper chromatogram with a weak solution of D-amino acid oxidase (Viobin Corporation, Monticello, Ill.). The chromatogram is then incubated in a moist chamber for several hours, dried, and sprayed with ninhydrin. A decrease in color, compared to an untreated control, indicates the presence and approximate quantity of the D-amino acid.

Contamination by the D-isomer in samples of supposedly pure L-isomers of cystine, hydroxyproline, proline, leucine, phenylalanine, tyrosine, tryptophan, etc., can be determined more accurately as follows: 1000 micromoles ( $\mu$ M.) of the L-isomer to be tested are placed in each of four Warburg vessels, and to each of these flasks 1  $\mu$ M. of the known D-optical enantiomorph (usually in the form of an aliquot of a larger volume) is added. To these four flasks, as well as to two others, buffer solution is added. In the sidearms of all six vessels D-amino oxidase solution is introduced. The flasks are tipped after the equilibration period and read at intervals until gas evolution or consumption is complete. This method is obviously applicable only where 1  $\mu$ M. of added susceptible isomer is readily and quantitatively oxidized in the presence of the 1000-fold amount of the resistant enantiomorph. As a rule, a considerable amount of the enzyme is employed. The 1000  $\mu$ M. of the L-isomer alone should consume less than 1 microatom of O<sub>2</sub>, while simultaneously the added 1  $\mu$ M. of D-isomer should be quantitatively oxidized as shown by the increment in the value over the L-isomer. All values are corrected for the enzyme blanks.

## QUANTITATIVE PAPER CHROMATOGRAPHY

### METHOD I: VISUAL COMPARISON

Casual inspection of a finished paper chromatogram reveals that both the intensity of color and the size of the spot vary with the quantity of the substance chromatographed. Thus, a reasonably accurate estimation of the quantity of a substance of unknown concentration may be obtained by developing on the *same* chromatogram a series of dilutions of the unknown and a series of dilutions of known concentrations. Then, where a spot of unknown concentration matches a spot of known concentration with respect to area and density of color, it may be assumed that the quantity of material in the "unknown" is equal to that of the standard. It is important that the *same volumes of solution* (both standard and unknown) be used throughout. If volumes of varying size are applied, then the areas of the spots will vary irrespective of the concentration of the substance under test. In practice, volumes of 1  $\mu$ l. to 10  $\mu$ l. are the most satisfactory.

<sup>26</sup> Kalyankar, G. D., and Snell, E. E., *Nature*, 180, 1069-1070, 1957.



### METHOD II: MAXIMUM COLOR DENSITY ON ONE-DIMENSIONAL CHROMATOGRAMS

During the investigations on amino acids and amines, it was observed that, because of the symmetrical nature of the color density curves, accurate results could be obtained by reading the concentration of the unknown material directly from calibration curves prepared from the maximum color densities of the standard solutions.

The quantitative estimation of colored substances directly on the paper after one-dimensional paper chromatography is more accurate than on two-dimensional chromatograms, as both the standards and unknowns are placed on the same sheet.

*Application of Spots.*—The method of application and the description of the types of pipets used are given in Block, Durrum, and Zweig.<sup>12</sup>

#### *Paper Chromatography.*

**Group A.**—Paper: Whatman No. 1. Size: 18 x 11 in. (long), ascending.

Solvent:  $C_6H_5OH:H_2O = 100$  ml. of 88% liquid phenol plus 20 ml. of  $H_2O$ .

A small quantity of 8-hydroxyquinoline is added to the phenol before the addition of the water. Beakers containing 10 ml. of 1% NaCN and 50 ml. of 3%  $NH_4OH$  are placed in box. Treat hydrolyzate spots with vapors of 1:4  $NH_4OH$  for 4 minutes.

Pipet: 2.5  $\lambda$  (if necessary 1  $\lambda$ ).

Length of Run: 23 cm.

Color Reagent: 0.25% ninhydrin in acetone.

Standards: 2, 4, 6, and 8  $\mu M$ ./ml. (if necessary 1  $\mu M$ .).

Unknown to Contain at Lowest Level:

Aspartic acid. . . . .	$R_f$	0.25	0.20–0.60 mg./ml.
Glutamic acid . . . . .	$R_f$	0.33	0.20–0.50 mg./ml.
Serine . . . . .	$R_f$	0.43	0.20–0.45 mg./ml.
Glycine . . . . .	$R_f$	0.48	0.12–0.30 mg./ml.
Threonine . . . . .	$R_f$	0.55	0.20–0.50 mg./ml.

**Group B.**—Paper: Whatman No. 1. Size: 18 x 11 inches (long), ascending.

Solvent: 1-Butanol:acetic:water = 450:50:125 vol./vol.

Pipet: 1  $\lambda$  (if necessary 2.5  $\lambda$ ).

Length of Run: 23 cm., dry, and rerun three times for 23 cm.

Color Reagent: Ninhydrin.

Standards: 2, 4, 6, and 8  $\mu M$ ./ml. (if necessary 1  $\mu M$ .).

Unknown to Contain at Lowest Level:

Cystine . . . . .	$R_f$	0.12	0.20–0.50 mg./ml.
Lysine. . . . .	$R_f$	0.18	0.25–0.60 mg./ml.
Histidine. . . . .	$R_f$	0.22	0.25–0.60 mg./ml.
Arginine. . . . .	$R_f$	0.26	0.25–0.70 mg./ml.
Alanine. . . . .	$R_f$	0.45	0.14–0.40 mg./ml.
Tyrosine. . . . .	$R_f$	0.60	0.25–0.65 mg./ml.
Phenylalanine. . . . .	$R_f$	0.80	0.30–0.70 mg./ml.
Isoleucine. . . . .	$R_f$	0.82	0.30–0.55 mg./ml.
Leucine. . . . .	$R_f$	0.85	0.30–0.55 mg./ml.

**Group B<sub>2</sub>.**—Iso-Amyl alcohol:pyridine:water:diethylamine = 50:50:35:2 vol./vol. in the presence of NaCN and aqueous phenol may be used for valine, methionine, tyrosine, isoleucine, leucine, and phenylalanine.

Length of Run: 23 cm., dry, and rerun twice for 23 cm.

**Group C.**—Paper: S. & S. 598. Size: 18 x 11 in. (long), ascending.

Solvent: 1-Butanol:acetic acid:water = 250:60:250 vol./vol.

Pipet: 5  $\lambda$  (if necessary 2.5  $\lambda$ ).

Length of Run: 25 cm.

Color Reagent: Diazotized sulfanilamide.

Standards: 2, 4, 6, and 8  $\mu$ M./ml.

Unknown to Contain at Lowest Level:

Histidine. . . . .	$R_f$	0.17	0.30-0.70 mg./ml.
Tyrosine. . . . .	$R_f$	0.40	0.20-0.70 mg./ml.

**Group D.**—Paper: S. & S. 598. Size: 18 x 11 in. (long), ascending.

Solvent: 1-Butanol:acetic acid:water = 450:50:125 vol./vol.

Pipet: 5  $\lambda$  (if necessary 2.5  $\lambda$ ).

Length of Run: 25 cm.

Color Reagent: Platinic iodide in acetone.

Standards: 1, 2, 4, and 6  $\mu$ M./ml. (if necessary 8  $\mu$ M./ml.).

Unknown to Contain at Lowest Level:

Methionine. . . . .	$R_f$	0.50	0.15-0.60 mg./ml.
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**Group E.**—Paper: Whatman No. 1. Size: 18 x 11 in. (long) or 18 x 20 in. (long), ascending.

Solvent: 1-Butanol:acetic acid:water = 450:50:125 vol./vol.

Pipet: 5  $\lambda$ .

Length of Run: 25 cm. for proline only; 46 cm. for proline and hydroxyproline.

Color Reagent: 0.2% isatin in acetone. After spraying, air dry, put sheets in oven at 70° to 76°C. for 10 minutes. Oven to be saturated with H<sub>2</sub>O vapors. For hydroxyproline, counterspray with color reagent F.

Standards: 1, 2, 4, and 6  $\mu$ M./ml.

Unknown to Contain at Lowest Level:

Hydroxyproline. . . . .	$R_f$	0.20	0.25-0.60 mg./ml.
Proline. . . . .	$R_f$	0.30	0.10-0.30 mg./ml.

**Group F.**—Paper: Whatman No. 1. Size: 18 x 11 in. (long), ascending.

Solvent: 2-Butanol: 3.3% NH<sub>3</sub> = 150:50 vol./vol.

Pipet: 2.5  $\lambda$  or 5  $\lambda$ .

Length of Run: 25 cm.

Color Reagent: *p*-Dimethylaminobenzaldehyde (1 g.) in a mixture of 10 ml. of concentrated HCl and 90 ml. of acetone. Prepare fresh just before use.

Standards: 2, 4, 6, and 8  $\mu$ M./ml.

Unknown to Contain at Lowest Level:

Tryptophan. . . . .	$R_f$	0.60	0.25-0.80 mg./ml.
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**Group G.**—Paper: Whatman No. 3. Size 18 x 22 in. (long), descending.

Solvent: 2-Butanol:3.3% NH<sub>3</sub> = 150:60 vol./vol. (3.3% NH<sub>3</sub> is prepared by diluting 60 ml. of 14.5-15.0 N NH<sub>4</sub>OH to 500 ml. with water). A marker of bromocresol purple placed at the starting line permits one to follow the development as the solvent is allowed to drip off the paper. Bromocresol purple moves slightly ahead of phenylalanine.

Pipet: 1.0  $\lambda$  or 2.5  $\lambda$ .

Length of Run: The bromocresol green should travel 45 cm. beyond the origin.

Color Reagent: Ninhydrin.

Standards: 1, 2, 4, 6, and 8  $\mu$ M./ml.

Unknown to Contain at Lowest Level:

Lysine . . . . .	0.25-0.60 mg./ml.
Arginine. . . . .	0.25-0.75 mg./ml.
Tyrosine . . . . .	0.25-0.65 mg./ml.
Valine . . . . .	0.20-0.50 mg./ml.
Methionine . . . . .	0.30-0.90 mg./ml.
Isoleucine . . . . .	0.30-0.60 mg./ml.
Leucine . . . . .	0.30-0.60 mg./ml.
Phenylalanine . . . . .	0.30-0.75 mg./ml.

**Replication.**—Four to six replicate spots are used for each level of standard and three or four levels of the unknown. Each sheet should have at least one application of each level of standard. The results are then averaged and the concentration of the unknown is read from the standard curve or calculated by the method of least squares. When the spots are applied 2 cm. apart, then 22 applications may be made on a single sheet 18 in. wide or 88 applications on 4 sheets in a single aquarium. It is advisable to use the same pipet for the application of standards and unknowns.

When six or more proteins are analyzed simultaneously, it is advisable to stagger the applications of standards and unknowns over the sheet in order to avoid having the same material always located near either end of the sheet.

**Method of Reading.**—All amino acids are roughly outlined in pencil using transmitted light (X-ray viewer). This facilitates centering each spot on the densitometer for the determination of the maximum color density. In the case of methionine (Group D), the amino acid is revealed by the bleaching of the platonic iodide reagent. The area of this bleached spot is proportional to the logarithm of the concentration of methionine provided that the volumes of the unknown and standard applied to the paper are identical.

**Calculations.**—The average densitometric readings of the standard solutions are used to prepare standard curves.

**Comment.**—The reproducibility of this procedure is in the order of  $\pm 5\%$  when two hydrolyzates of the same protein are analyzed on the same chromatograms. Further discussion of the errors is given in Block, Durrum, and Zweig.<sup>12</sup> Fowler<sup>27</sup> has reported that the logarithm of the spot content is a constant function of the logarithm of the spot length on 5-mm. strips of paper.

### METHOD III: QUANTITATIVE DETERMINATION OF DNP AMINO ACIDS

**Dinitrophenylation.**<sup>28</sup>—Dinitrophenylation is effected quantitatively by stirring an aqueous solution of the amino acids (20 to 50  $\mu$ M. in 3 ml.) with a slight excess of 1-fluoro-2,4-dinitrobenzene (FDNB) for 80 minutes at pH 9.0 and 40°C., the pH being maintained at this value throughout this period by intermittent additions of standard alkali. Excess FDNB is then extracted with ether, the solution is acidified, and the DNP amino acids are extracted into ether (5 x 5 ml.). The aqueous solution, which contains DNP arginine and  $\alpha$ -DNP-histidine, is diluted to 10 ml.

<sup>27</sup> Fowler, H. D., *Nature*, 168, 1123-1124, 1951.

<sup>28</sup> Levy, A. L., *Nature*, 174, 126-127, 1954.

## CHROMATOGRAPHY

*Apparatus and Reagents.* Paper.—Whatman No. 1.

Solvents.—Toluene:chloroethanol:pyridine:0.8 N ammonia = 10:6:3:6 vol./vol. and 1.5 M phosphate buffer, M  $\text{NaH}_2\text{PO}_4$  plus 0.5 M  $\text{Na}_2\text{HPO}_4$ .

*Procedure.*—A 2-ml. aliquot of the ether solution and a 1.0 ml. aliquot of the water solution are next applied to adjacent corners of an  $18\frac{1}{4} \times 22\frac{1}{2}$  in. sheet of Whatman No. 1 filter paper, which is then irrigated by the ascending procedure with the toluene:chloroethanol:pyridine:ammonia. The chromatogram is dried for 3 to 4 hours at  $40^\circ\text{C}$ ., and the spots due to DNP-arginine and  $\alpha$ -DNP-histidine are excised at this point. The paper is then run in the second dimension by the descending procedure with aqueous phosphate buffer. All the ether-soluble DNP-amino acids are thereby separated except DNP-leucine and isoleucine. The positions of DNP-tryptophan and di-DNP-histidine coincide, but this does not present a difficulty in practice, since the former amino acid is not normally present in acid hydrolyzates and the latter amino acid is determined as its mono-DNP derivative.

The spots are cut out and dropped into a set of labeled test tubes; three blanks are also cut from each sheet. Four milliliters of water are pipetted into each of the tubes, which are then placed in a water bath at  $55^\circ$  to  $60^\circ\text{C}$ . for 15 minutes to allow complete elution of the color. After an additional 15 minutes to allow the solutions to cool to room temperature, they are successively decanted into a 1-cm. quartz cuvet, and the optical densities at 360 m $\mu$  (385 m $\mu$  in the case of DNP-proline) are read in the Beckman Model DU spectrophotometer against a water blank. The optical density reading of the tubes containing blank paper is 0.001 to 0.002 per square centimeter, and the appropriate corrections are made for each spot according to its estimated size.

*Calculations.*—The resulting optical density ratios of the DNP-amino acids are converted to molar ratios by multiplying by the following factors, which, within the accuracy of the method ( $\pm 4\%$ ), are independent of the composition of the mixture analyzed: Asp, 0.99; Glu, 0.94; CysS, 0.56; Ser, 0.97; Thr, 1.02; Gly, 1.03; Ala, 1.09; Pro, 0.93; Val, 0.99; Met, 1.21; Leu and Isoleu, 1.10; Phe, 1.03; Tyr, 1.54; Lys, 0.64; His, 1.62; Arg, 1.06. When the chromatograms are run in triplicate, the molar ratios are found to be reproducible to within 2 to 3%. Tyrosine is subject to rather wider variation.

## COLUMN CHROMATOGRAPHY ON ION EXCHANGE RESINS

*Introduction.*—In 1951 Moore and Stein<sup>29</sup> described a procedure for the chromatographic separation of mixtures of amino acids by elution analysis on synthetic ion exchange resin. The procedure permits accurate determination of the commonly occurring amino acids in acid hydrolyzates of proteins.

Primary emphasis will be placed on the experimental details of the ion exchange method and its use in amino acid analysis of proteins. Only a few pertinent articles will be cited as illustrative of the earlier developments in column chromatography of amino acids. Reviews of the subject by Wieland<sup>30</sup> (1943), Martin and Syngé<sup>31</sup> (1945), Tiselius<sup>31</sup> (1947), Block<sup>32</sup> (1949), and

<sup>29</sup> Moore, S., and Stein, W. H., *J. Biol. Chem.*, 192, 663-681, 1951.

<sup>30</sup> Wieland, T., *Die Chemie*, 56, 213-215, 1943.

<sup>31</sup> Tiselius, A., *Advances in Protein Chem.*, 3, 67-93, 1947.

<sup>32</sup> Block, R. J., *The Separation of Amino Acids by Ion Exchange*, in Nachod, F. C. (ed.), *Ion Exchange*, Academic Press, Inc., New York, pp. 295-314, 1949.

Samuelson<sup>33</sup> (1953) may be consulted for additional information. Kitchener<sup>34</sup> (1957) has presented an excellent review of ion exchange processes.

### QUANTITATIVE DETERMINATION OF AMINO ACIDS

**Principle.**—A mixture of amino acids (*ca.* 2 mg.) is added to a 0.9- by 150-cm. column of Amberlite IR-120. The neutral and acidic amino acids are eluted by buffers. The effluent is collected by means of an automatic fraction collector in 2-ml. portions in optically calibrated tubes. The amino acids emerge in a definite sequence, well separated from each other. Ninhydrin reagent is added to each tube for spectrophotometric determination of amino acid concentration. Summation of the quantities of amino acid found in the appropriate group of tubes gives the yield of each amino acid. The recoveries are quantitative ( $100 \pm 3\%$  on the average). The basic amino acids are determined quantitatively with equal accuracy in a separate experiment on a 0.9- by 15-cm. column of the resin.<sup>29,35</sup>

**Equipment and Reagents.** **Fraction Collector.**—Any one of several commercial fraction collectors may be used. A capacity of two hundred 18- by 150-mm. tubes is desirable.

**Spectrophotometer.**—An instrument such as the Coleman Junior or the Beckman Model B spectrophotometer, wherein direct readings of optical density in 18- by 150-mm. test tubes may be made, is needed.

**Calibration of Test Tubes.**—A matched set of at least 100 test tubes (18 by 150 mm., without lips) should be calibrated as follows: Prepare a solution of methyl red in 0.03 N HCl of such strength as to give a reading at 525  $m\mu$  of 0.6 to 0.7 on the optical density scale against a water blank.<sup>36</sup> Add 5 to 10 ml. of the solution to each tube, and select only those tubes which read within 0.005 unit of the same density value. Mark permanently the side of the tube facing the light source and align the tube in the same way each time it is read. Number the selected tubes with a glass marking tool.

Aluminum caps are convenient covers for the tubes during the course of analysis.

**Boiling Water Bath.**—This bath, for ninhydrin color development, should be large enough to hold a rack of 50 tubes immersed in vigorously boiling water to a depth of about 5 cm.

**Constant Temperature, Circulating Water Bath.**—This is required to maintain the temperature of the column at  $50^\circ$  and  $75^\circ \pm 0.5^\circ\text{C}$ .

**Pipetting Machine.**—Although such a device is not essential, it saves much time in dispensing reagents.

**Buffers.**—The buffers are prepared in quantity and are stored in the cold with thymol or with 0.1% wt./vol. or 0.05% wt./vol. phenol.

Sodium citrate buffers of different pH may be prepared from data contained in Table 27-2.

Thiodiglycol (TG) is added as an antioxidant to prevent losses of methionine. It may be purchased in purified form from Pierce Chemical Company (Rockford, Ill.) or purified by the redistillation under reduced pressure of Kromfax solvent

<sup>33</sup> Samuelson, O., *Ion Exchangers in Analytical Chemistry*, John Wiley and Sons, Inc., New York, 1953.

<sup>34</sup> Kitchener, J. A., *Ion-Exchange Resins*, Methuen, London, 1957.

<sup>35</sup> Moore, S., Spackman, D. H., and Stein, W. H., *Anal. Chem.*, **30**, 1185-1190, 1958.

<sup>36</sup> Instead of the methyl red solution, the more stable solution of 0.12 M  $\text{CoCl}_2 \cdot \text{H}_2\text{O}$  in 0.25 N HCl at a wavelength of 515  $m\mu$  is preferable for these calibrations (Dr. W. G. Gordon, unpublished).

TABLE 27-2. PREPARATION OF SODIUM CITRATE BUFFERS

pH	Sodium Concentration <i>N</i>	Citric Acid H <sub>2</sub> O g.	NaOH (97%) g.	HCl (conc.) ml.	Final Volume liters	Phenol Added to Final Volume g.	TG ml., l.	BRIJ ml., l.
3.25 ± 0.01	0.20	840	330	426	40	40	10	5
4.25 ± 0.02	0.20	840	330	188	40	40	10	5
5.28 ± 0.02	0.35	491	288	136	20	20	—	5
4.26 ± 0.02	0.38	532	312	307	20	20	—	5
6.50 ± 0.05	0.28	133	78	6.3	5	5	—	5

(Carbide and Carbon Chemicals Corporation) or technical 2,2'-thiodiethanol (Eastman). BRIJ 35 (Atlas Powder Company, Wilmington, Del.) is a neutral, stable detergent, which permits faster flow during elution. Dissolve 50 g. of BRIJ 35 in 100 ml. of H<sub>2</sub>O for the stock solution. Both TG and the BRIJ 35 solution are added in the stated quantities to several liters of the buffer shortly before use, not to the 40-l. quantities that are to be stored. BRIJ 35 can be omitted if it interferes with the action of the fraction collecting device.

If adjustment of pH is necessary, the addition of 1 ml. of 50% NaOH or 2 ml. of concentrated HCl to the final volumes listed above causes a change of about 0.01 pH unit.

Buffer for immediate use is kept in a 500-ml. separatory funnel fitted with a stopcock clamp and connected to the top of the column as previously described. In order to prevent the formation of bubbles in the resin bed, which would occur as a result of the release of air when the buffers are heated to 50°C., a 500-ml. quantity of the buffer is brought to a boil and added while hot to a separatory funnel. About 50 ml. of mineral oil is layered over the buffer. A long-stem funnel is employed to introduce the buffer below the level of the oil. Individual separatory funnels are reserved for each of the three buffers and for the 0.2 *N* NaOH (see below).

**Methyl Cellosolve.**—The reagent (peroxide-free grade) should be clear when mixed with an equal volume of water (test with 10% aqueous KI). Storage in the presence of zinc-copper couples will keep the reagent peroxide-free.

**Ninhydrin Solution.**<sup>37, 38</sup>—A 4 *N* sodium acetate buffer, pH 5.51 ± 0.03, is prepared from 2720 g. of NaOAc·3H<sub>2</sub>O in 2 l. of water, 500 ml. of glacial acetic acid, and water to 5 l. Final adjustment of the pH is made with solid NaOH or glacial acetic acid.

Dissolve 20 g. of ninhydrin and 3 g. of hydrindantin in 750 ml. of methyl Cellosolve, and add 250 ml. of pH 5.5 buffer. Store in a dark bottle under N<sub>2</sub>.

**Diluent Solution.**—Ethanol:water = 1:1 vol./vol.

<sup>37</sup> Moore, S., and Stein, W. H., *J. Biol. Chem.*, 176, 367-388, 1948.

<sup>38</sup> Moore, S., and Stein, W. H., *J. Biol. Chem.*, 211, 893-906, 1951.

**Resin.**—The finely ground sodium salt of Amberlite IR-120 (Rohm and Haas Company, Type II, finer than 200 mesh) is used.

One pound of the resin usually supplies enough material for two 0.9- by 150-cm. columns and one 0.9- by 15-cm. column, but it is desirable to have on hand at least 2 pounds of starting material.

**Separation of Particles of Appropriate Size.**<sup>39</sup>—One pound of the dry sodium salt of the resin, as purchased, is transferred in a hood to a jar containing about 10 l. of water. Resin present in any foam that remains after the initial stirring of the mixture can be transferred to a beaker, treated with a little acetone, and added back to the main suspension. After thorough distribution of the resin in the water, the mixture is allowed to settle for about 6 hours. The supernatant suspension, which contains very fine particles of resin, is withdrawn by suction. The resin is suspended and resettled 3 or 4 times. The product is then transferred to a large Buchner funnel and washed slowly with 2 l. of 1 *N* HCl and 500 ml. of water. The moist resin is suspended in 2 l. of 2 *N* NaOH, and the mixture is heated on the steam bath for 1 hour. The resin is finally collected on a Büchner funnel and washed with water until neutral.

The final test of the suitability of a resin is the performance of a column prepared from it. If a column is too tight, it may be necessary to repeat the hydraulic fractionation in order to remove a small percentage of the finest particles from the resin. If the resolving power of the column is deficient, some of the coarser particles need to be removed.

Fractions of resin that are to be stored for later use may be suspended in 0.2 *N* NaOH and kept in polyethylene bottles at 4°C. If moist neutral suspensions are stored at room temperature, contamination by molds may occur.

**Chromatograph Columns.**—Zechmeister-Cholnoky type, with ground joints and coarse sintered glass plates; glass tubing 0.9 cm. inner diameter, 1.5 to 2 mm. wall thickness; length of tubes for 150-cm. resin column, 166 cm., and for 15-cm. resin column, 30 cm.

The tubes are jacketed to permit temperature control by circulation of water from the constant temperature bath.

**Preparation of Resin Columns.**—The 150-cm. column to be used with fraction collectors is poured with resin of the powdered Amberlite IR-120. The average diameter of the particles in this fraction is  $56 \pm 9$  microns. About 100 ml. of settled resin are required for each 150-cm. column.

The resin to be used is washed on a Büchner funnel with 1 liter of 4 *N* HCl per 200 to 300 ml. of settled resin in order to remove metal ions. After a wash with water, 2 *N* NaOH is percolated through the resin cake until the filtrate is strongly alkaline. The sodium salt of the resin is washed with water and then with several hundred milliliters of 0.2 *N* buffer at pH 4.25 without BRIJ 35 or thiodiglycol until the filtrate is about pH 4. The columns are poured with a suspension of resin in this buffer. The composition of the slurry should be such that the volume of the supernatant buffer is twice that of the settled resin. If the handling of the resin has caused the formation of small amounts of very finely divided material, the resin should be settled 2 or 3 times from about 6 to 8 volumes of the buffer until the supernatant liquid is practically free of suspended particles.

<sup>39</sup> Hamilton has described a useful hydraulic procedure for separating and grading the resin particles. See Hamilton, P. B., *Anal. Chem.*, 30, 914-919, 1958.

To prepare a column for use, suspend the washed resin in about twice its volume of buffer, pH 4.25 without detergent. Allow it to settle and remove any bubbles by gentle stirring. Pour the slurry into the chromatograph tube in 5 or 6 portions of about equal volume using a funnel with a bent, constricted tip to direct the flow of slurry against the side of the tube. Before the first section is poured, the outlet of the tube is closed. As soon as the slurry of resin has been poured in, the outlet is opened and about 2 cm. of resin bed are allowed to form under gravity flow. Air pressure of 30 cm. of mercury is then applied at the top of the tube. The pouring is done at room temperature. After the resin has settled to constant height, all of the supernatant buffer is withdrawn by suction and the next section is poured on top of the firm surface. After the third section has been added, a 0.9- by 40-cm. extension tube is attached to the top of the chromatograph tube by means of a butt joint held by about 0.8-cm. i.d. rubber tubing (or through  $\frac{1}{8}$ " semiball joints). The final height of the resin should be several centimeters greater than 150 cm. in order to allow for some further packing during operation.

Before use, a new 150-cm. column should be washed with 0.2 *N* NaOH and equilibrated with boiled buffer at pH 3.25, as described below for the regeneration of the columns. Both operations are carried out at room temperature before the temperature is raised to 50°C. The rate of flow at 50°C. should then be checked. If the column is too tight to permit delivery of 12 ml. of effluent per hour under 20 to 40 cm. of pressure, the resin is withdrawn from the tube and some of the finest particles must be removed from the resin by settling or by refractionation, and the column repoured. If the column permits a much faster flow rate than 12 ml. per hour at 20 cm. of pressure, a test chromatogram may be run, but the column is likely to be too loose to give the desired resolving power. Flo-tation to remove more of the larger particles would then be required. Once a column of resin possessing the desired particle size is obtained, it can be used indefinitely; adjustment of the particle size distribution is thus not a recurring task.

The 15-cm. columns are poured similarly, in one or two sections, with resin that has been slurried in 0.35 *N* buffer at pH 5.28. All columns should be prepared in buffer with the same ionic strength as that with which they will be operated. Since the resistance to flow through the 15-cm. columns is never great, it is advantageous to pour these from fine resin (average diameter 40 microns) in order to obtain high resolving power. The column is equilibrated before use with boiled buffer that contains BRIJ 35.

Attach a separatory funnel (about 300-ml. capacity) as a reservoir for appropriate buffer to the column with a length of plastic tubing so that the funnel may function as a leveling bulb. Run about 100 ml. of buffer through the column. It is then ready for use.

*Procedure for Photometric Ninhydrin Method.*<sup>37, 40</sup>—To 2 ml. of amino acid solution at about pH 5.0 add 1 ml. of ninhydrin solution. Place aluminum caps on the

<sup>40</sup> Rosen suggests the following procedure: To 1 ml. of sample, containing 0.02–0.4  $\mu$ M. of amino acid, add 0.5 ml. of NaCN-acetate buffer (270 g. Na acetate $\cdot$ 3H<sub>2</sub>O, 200 ml. of H<sub>2</sub>O, and 50 ml. of acetic acid, dilute to 750 ml. with water, then add 1.5 ml. of 0.01 *M* NaCN) and 0.5 ml. of 3% wt./vol. ninhydrin in methyl Cellosolve. Develop the color by heating in a boiling water bath for 15 minutes and immediately add 5 ml. of 50% vol./vol. 2-propanol. The colored solution can be further diluted with 50% vol./vol. 2-propanol if desired. See Rosen, H., Arch. Biochem. Biophys., 67, 10–15, 1957.



tubes and mix by gentle shaking. Heat in *vigorously boiling* water bath for 15 minutes. Allow to cool for a few minutes and add 5 ml. of 50% vol./vol. ethanol. Shake well for 1 minute to remove the reddish hydrindantin color. Read in the spectrophotometer beginning at about 15 minutes after removal from the bath, using 440 m $\mu$  for proline and hydroxyproline and 570 m $\mu$  for all other amino acids. Read reagent blanks against the diluent. Select average reagent blank, set instrument to zero on this blank, and read unknown. The reagent blank reading should be about 0.15 to 0.20 on the optical density scale. Analyses should be run in groups of not more than 50 tubes to permit readings to be completed within 1 hour after the heating period; during this time readings remain essentially constant.

When optical density values at 8.0 ml. total volume are too high for accurate reading, further additions of one, two, or three 5-ml. portions of diluent solution are made, the average reagent blank is diluted likewise, and readings are taken at 13, 18, or 23 ml. If readings at 23 ml. are still too high, aliquots of unknown and blank are pipetted into other calibrated tubes and further dilutions are made.

**Leucine Calibration Curve.**—On a molar basis the amino acids do not give the same color yield in the ninhydrin reaction. However, only one calibration curve is required because accurate color yields relative to leucine have been established. Relative to the leucine color value at 570 m $\mu$  taken as 100, the color yields per mole for other amino acids are: <sup>38</sup> Hydroxyproline 8 (410  $\lambda$ ); aspartic acid 91; threonine 91; serine 95; glutamic acid 99; proline 22.5 (410  $\lambda$ ); glycine 95; alanine 97; half-cystine 55; valine 97; methionine 102; isoleucine 100; tyrosine 100; phenylalanine 100; tryptophan 91; histidine 102; lysine 110; ammonia *ca.* 97; and arginine 101. Spectrophotometer readings taken at 440 m $\mu$  for proline (and for hydroxyproline, if present) are first converted to "micromoles leucine," using the leucine calibration curve at 570 m $\mu$  employed for the other amino acids; these values are then divided by the above color yields to give micromoles of proline or hydroxyproline.

Prepare a calibration curve, plotting micromoles of leucine against optical density, with a sample of leucine of established purity. Use aqueous solutions of the amino acid at several different levels of concentration, within the range 0.05 to 0.20  $\mu$ M. of leucine per 2-ml. aliquot. This is a convenient range for ninhydrin color development by the above procedure in a total volume of 8 ml. Once the standard curve has been confirmed by replicate experiments, a standard table relating optical density to micromoles of leucine may be prepared, and from these figures further tables may be calculated of total volumes of 13, 18, and 23 ml. for higher concentrations of amino acid.

**Operation of 150-Cm. Columns.**—With the prepared column in place above the fraction collector,<sup>41</sup> begin circulating water at 5°C. through the jacket about an hour before the start of a run. Heat to boiling about 300 ml. of buffer of pH 3.25 to free it of dissolved air, pour the warm buffer into the separatory funnel, and cover the solution with a thin layer of mineral oil. Add the sample of amino acid solution to the column with a 1- or 2-ml. pipet with bent tip so as not to disturb the surface of the resin. When the sample is drained into the resin, wash down in the same way with 3 successive 0.3-ml. portions of buffer, and finally

<sup>41</sup> If the collector is of the Technicon type, with the tubes housed in an enclosed chamber, it is well to circulate a slow stream of ammonia-free air through the chamber; shallow dishes containing citric acid solution may also be used on top of the rack to minimize absorption of ammonia by the acidic eluate.

layer about 2 ml. of the buffer above the surface of the resin. Do not allow the surface of the resin to dry out during these operations. pH of the amino acid solution should be more acid than that of the buffered column, about 2.5 to 3.0 being optimal. Usually, a charge of about 1 to 2 mg. of total amino acid mixture is introduced for a chromatogram, but several times this quantity is permissible and is recommended for more accurate determination of amino acids present in small concentration.

Connect the buffer reservoir and adjust the flow rate of solvent through the column to about 4 ml. per hour by adjusting the height of the separatory funnel or by using slight air pressure. Collect the effluent in 2-ml. fractions.

An eluate at pH 4.25 is introduced at a time designed to allow valine to emerge with the new buffer. The change is made at an effluent volume 2.15 times that at which the aspartic acid peak has emerged, or about 260 ml. At a flow rate of 12 to 14 ml. per hour, this point will have been reached on the day after the column has been started. By the following morning, tyrosine and phenylalanine will have emerged. The amino acids may all be eluted somewhat more slowly or more rapidly if the chromatograph tube has a diameter slightly different from 0.9 cm.

The position of cystine is extremely sensitive to pH, and it is necessary for the user to determine by experiment what the exact pH value of the initial buffer should be so that cystine will be eluted about midway between alanine and valine. Subsequent lots of the buffer should be adjusted as closely as possible to this pH value, checking with a sensitive pH meter and using as reference buffer standard 0.05 M potassium acid phthalate at pH 4.00.

To prepare the 150-cm. column for reuse, the basic amino acids that are retained by the resin are eluted with 0.2 N NaOH (containing 5 ml. of BRIJ 35 solution per liter). The alkali can be allowed to run through under gravity flow overnight, or under a few centimeters of pressure until the visible advancing front of NaOH is more than halfway down the column. The NaOH solution is not boiled or stored under oil; the funnel should be stoppered when not in use, so as to minimize uptake of  $\text{CO}_2$ . The column is re-equilibrated for the next analysis by passing through it overnight at room temperature or 50°C. about 120 ml. of buffer at pH 3.25. If two 150-cm. columns are on hand, one can always be ready for use.

If the surface of the column becomes clogged at any time, remove the top centimeter of resin and replace it with fresh resin. Never allow the resin to dry out.

**Operation of 15-Cm. Columns.**—A 15-cm. column can be operated on the fraction collector during the day, after a 150-cm. column has been removed. For the determination of the basic amino acids, the aliquot taken is equal to or one-half the size of the sample used for the 150-cm. column. The pressure used during the addition of the sample should not be more than 10 cm. Elution is carried out at 50°C. with a buffer at pH 5.28 and at a rate of 25 to 30 ml. per hour. The analysis is complete after about seventy 2-ml. fractions have been collected, which requires only 5 to 6 hours. By the elution of lysine, histidine, ammonia, and arginine with a single buffer, it is possible to obtain a constant base line throughout the chromatogram. It is important that the buffer used to fill the top part of the chromatograph tube after the sample has been added should be drawn from the separatory funnel containing the buffer with which the column is to be operated. Even a few milliliters of buffer that contain a concentration of ammonia higher or lower than the main lot can give rise to a shoulder or valley following the ammonia peak. The columns can normally be used repeatedly without regeneration, since the most samples do not contain any ninhydrin-positive constituents with a

greater retardation than arginine. Regeneration, if required, can be accomplished with 10 ml. of 0.35 *N* NaOH containing BRIJ 35, after which 80 ml. of the pH 5.28 buffer should be run through before the column is reused.

The position of histidine is fairly sensitive to pH, and adjustment of the buffer at pH 5.28 may be required to center the peak between those of lysine and ammonia.

**Analysis of Collected Fractions.**—Develop the ninhydrin color in 50 tubes at a time.

Add ninhydrin and develop color as described. In making the optical density readings it is important to choose the proper blank against which amino acid concentration is read. Usually a representative blank can be chosen from the valleys in the curve. Select the blank for methionine, isoleucine, and leucine after the leucine peak.

**Calculation of Results.**—Since the leucine calibration curve is plotted for volumes of 8.0 ml., volume corrections may be required in the calculation of results. Although the fraction collector is set to deliver samples of  $2.0 \pm 0.1$  ml., it is advisable to spot check its performance by weighing every tenth tube in a run before and after a fraction has been collected. An approximate volume correction can then be made for any deviation from 1.0 ml. In addition, a correction can be made for the volume of acid or alkali used to adjust the solutions to pH 5. Because optical density readings are made at a minimal volume of 8.0 ml., these volume corrections are important only when maximum accuracy is sought.

Corrected optical densities are converted to "micromoles leucine" and the values for each peak are integrated or the sum of all the readings is used. Use of the appropriate color yield then converts these figures into micromoles of amino acid.

**Preparation of Samples for Chromatograms.** **Alanine-Cystine-Valine Mixture.**—The order and position of amino acid peaks emerging from the column, while quite reproducible under the conditions specified, are rather sensitive to changes of pH and ionic strength of the buffers. The position of the cystine peak varies markedly with small changes in pH of this buffer. It is necessary, therefore, to check the performance of the buffer before use in analysis.

Prepare a solution in dilute HCl of 4  $\mu$ M. of alanine, 6  $\mu$ M. of valine, and 2  $\mu$ M. of cystine per milliliter. Mix 1 ml. of the solution with 1 ml. of buffer and add 1 ml. of the mixture to the 100-cm. column. Run the chromatogram with the buffer until valine is eluted (about 340 ml.). If the results show the peaks to be separated poorly, adjust the pH so that the cystine peak will be better positioned midway between the alanine and valine peaks, and repeat the experiment.

**Amino Acid Mixtures.**—It is important to run preliminary chromatograms with known mixtures of pure amino acids in order to establish a routine procedure whereby the reproducibility and accuracy inherent in the method can be realized. Unknown mixtures should then be analyzed in precisely the same way.

Prepare accurately a known mixture of amino acids and  $\text{NH}_4\text{Cl}$  simulating the composition of a protein hydrolyzate. Tryptophan may be omitted because the present method was developed for acid hydrolyzates. Cysteine may also be omitted because, if present, it is gradually oxidized and does not give a peak. The amounts of the 17 amino acids and  $\text{NH}_4\text{Cl}$  to be weighed out are determined by the following considerations. A total of about 1 g. of amino acids is dissolved in 1.5 ml. of 6 *N* HCl and made to 10 ml. with 10% vol./vol. 2-propanol. This solution is stored in the cold. An aliquot of the solution is diluted 1 to 10 with pH 3.25 buffer for the 150-cm. column, or with pH 5.3 buffer for the 15-cm. column. A

0.2-ml. aliquot of the resulting solution will then contain about 2 mg. of total amino acids, a quantity suitable for analysis.

Recoveries of  $100 \pm 3\%$  should be obtained for the majority of amino acids and ammonia. The recovery of methionine is 95%; a small conversion to the sulfoxide occurs during the chromatography.

*Quantitative Determination of Amino Acids by Automatic Methods.*—Moore, Spackman, and Stein<sup>42, 43</sup> have adapted their ion-exchange method to automatic equipment which permits a complete amino acid analysis to be performed in 24 hours. This equipment is available from Phoenix Instrument Company, Philadelphia, Pa., and from Beckman Instrument, Inc., South Pasadena, Calif. Hannig<sup>44</sup> has developed instrumentation for the automatic analysis of amino acids which is sold by Bender and Hobein, Munich, Germany. The method of Piez and Morris<sup>45</sup> employing a single column of Dowex 50X12 resin and a variable gradient elution device for the buffers has been adapted by the Technicon Corporation, (Chauncy, N. Y.) for automatic analysis on ChromoBead resin. The Technicon Autoanalyzer and the Bender and Hobein instrument are, at the present writing (1962), considerably cheaper than the equipment sold by Phoenix or by Beckman. Simmonds<sup>46</sup> has also described semi-automatic equipment for amino acid analysis.

It should be pointed out that the determination of amino acids using either the original Moore and Stein methods<sup>29, 35</sup> or the more recent automatic equipment requires considerable experience, and is advised only when a large number of samples are to be analyzed.

## COLORIMETRIC METHODS

When it is desired to determine a few amino acids only, the colorimetric procedures given below are often easier to carry out than chromatographic or microbiological methods. A single example is given for each amino acid; other procedures are described in Block and Bolling<sup>5</sup> and by Block and Weiss.<sup>4</sup>

### ARGININE by Sakaguchi's method<sup>40</sup>

*Procedure.*—Mix  $x$  ml. of hydrolyzate +  $5x$  ml. of  $H_2O$  + 1 ml. 10% wt./vol. NaOH + 0.1% wt./vol. of  $\alpha$ -naphthol. Cool in running water for 5 minutes. Add 1 ml. of diluted NaOCl (proper dilution estimated by trial and error) with a rapid delivery pipet. Read color in the colorimeter. Using three different sized aliquots of the hydrolyzate, plot the apparent arginine concentration vs. the concentration of the protein. The true arginine value is obtained by extrapolation to zero hydrolyzate.

### HISTIDINE by the Knoop-Kapeller-Adler Reaction<sup>47, 48</sup>

*Reagents.* Sulfuric Acid, 1.9–2.0 *N*.

*Bromine.*—Dissolve 0.5 ml. of  $Br_2$  in 50 ml. of *tert*-butanol + 50 ml. of 0.6% wt./vol. KBr. Store in dark at  $-4^\circ$  to  $5^\circ C$ . Do not keep longer than 4 weeks.

<sup>42</sup> Spackman, D. H., Stein, W. H., and Moore, S., *Anal. Chem.*, 30, 1190–1206, 1958.

<sup>43</sup> Hannig, K., *Clin. Chim. Acta*, 4, 51–57, 1959.

<sup>44</sup> Piez, K. A., and Morris, L., *Anal. Biochim.*, 1, 187–201, 1960.

<sup>45</sup> Simmonds, D. H., *Anal. Chem.*, 30, 1043–1049, 1958.

<sup>46</sup> Salo, T. P., *Arch. Biochem.*, 24, 25–30, 1949.

<sup>47</sup> Hunter, A., *J. Biol. Chem.*, 196, 589–598, 1952.

<sup>48</sup> Hunter, A., *J. Biol. Chem.*, 216, 391–394, 1955.

**Sodium Arsenite.**—Dissolve 3 g.  $\text{As}_2\text{O}_3$  in 10 ml. of 10% wt./vol. NaOH and dilute to 100 ml.

**Copper Acetate.**—To 90 ml. of  $\text{H}_2\text{O}$  add 2.1 ml. of glacial acetic acid, 0.26 ml. of 1% wt./vol.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and dilute to 100 ml. Then add 100 g. of  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ . Volume = 172 ml. containing 9.6  $\mu\text{g}$ .  $\text{CuSO}_4$  per ml.

**Procedure.**—To 5 ml. of solution containing 0.12 to 0.28  $\mu\text{g}$ . of histidine, add 0.5 ml. of 2 N  $\text{H}_2\text{SO}_4$ . Mix, warm to  $25^\circ\text{C}$ ., and in a dark room add 0.25 ml. of bromine reagent. Stopper and place in dark at  $25^\circ\text{C}$ . for  $2\frac{1}{2}$  hours. Add five or six drops (0.25 ml.) of arsenite reagent, then add rapidly with shaking 1.2 ml. of acetate reagent. After 14 minutes at  $25 \pm 0.2^\circ\text{C}$ ., dilute with water at  $10^\circ\text{C}$ . to 10 ml., and read with 510-m $\mu$  filter against reagent blank. The red pigment adsorbs on the glass and requires  $\text{HNO}_3$  to clean.

### LYSINE<sup>49</sup>

**Procedure.** Preparation of Hydrolyzate and Adsorption of Bases.—A sample of protein is hydrolyzed with HCl in the usual fashion; the hydrolyzate is adjusted to pH 5 with NaOH and decolorized. An aliquot of hydrolyzate equal to 30 mg. of protein in 25 ml. of water is shaken with 1 g. of Permutit previously treated with 0.33 N NaOH and then washed free of alkali with distilled water. The adsorption is repeated with a fresh 1-g. portion of Permutit. The Permutit is removed and washed thoroughly with water. The adsorbed basic amino acids are eluted with five 10-ml. portions of 0.33 N NaOH.

**Development of Color.**—Aliquots containing 0.1 to 0.7 mg. of lysine are placed in 22- by 200-mm. test tubes graduated at the 25-ml. mark. The tubes are cooled in an ice bath for 15 minutes. Then saturated  $\text{Br}_2$  water is added drop by drop until a permanent color is seen. Add three drops excess and keep in the ice bath 30 minutes longer. The excess  $\text{Br}_2$  is removed by aeration for 10 minutes and the aerating tubes are rinsed down with 4.5 ml. of water. The tubes are then placed in a water bath at  $60^\circ\text{C}$ . for 5 minutes and 7.5 ml. of 20% wt./vol.  $\text{Na}_2\text{CO}_3$  (at  $60^\circ\text{C}$ .) are added. The tubes are removed one at a time and 2.5 ml. of Folin's phenol reagent<sup>5</sup> are added with mixing. After cooling to room temperature, the solutions are diluted to 25 ml. and read in a colorimeter with 680-m $\mu$  filter in 30 minutes.

**Comment.**—Arginine and  $\text{NH}_4\text{Cl}$  do not give a color, but if histidine is present, a correction must be employed.

### TYROSINE AND TRYPTOPHAN<sup>50, 51</sup>

**Reagents.** Sulfuric Acid, 5 N.—25 g.  $\text{H}_2\text{SO}_4$  per ml.  $\text{H}_2\text{O}$ .

**Precipitation Reagent.**—Dissolve 75 g.  $\text{HgSO}_4$ , 55 g.  $\text{HgCl}_2$ , and 70 g.  $\text{Na}_2\text{SO}_4$  in a mixture of 850 ml. of water and 125 g. of  $\text{H}_2\text{SO}_4$  (68 ml.  $\text{H}_2\text{SO}_4$ , sp. gr. 1.84). Dilute to 1 liter.

**Washing Reagent.**—Dilute the precipitation reagent with an equal volume of N  $\text{H}_2\text{SO}_4$ .

**Color Reagent.**—Dissolve 12 g. of  $\text{HgSO}_4$  and 9 g. of  $\text{HgCl}_2$  in a mixture of 600 ml. of  $\text{H}_2\text{O}$  and 100 g. of  $\text{H}_2\text{SO}_4$  (54 ml.  $\text{H}_2\text{SO}_4$ , sp. gr. 1.84), then add 500 g. more of  $\text{H}_2\text{SO}_4$  (270 ml.). Cool, dilute to 1 liter.

<sup>49</sup> Kibrick, A. C., Arch. Biochem., 20, 22-24, 1949.

<sup>50</sup> Tyrosine and tryptophan can also be determined by their absorption of ultraviolet light. See footnote 51.

<sup>51</sup> Bencze, W. L., and Schmid, K., Anal. Chem., 29, 1193-1196, 1957.

**Procedure.** Hydrolysis.—Use 1 to 3 ml. of 5 *N* NaOH per 100 mg. of protein in an oil bath at 110° to 125°C. for 5 hours. Neutralize the hydrolyzate with 3 ml. of 7 *N* H<sub>2</sub>SO<sub>4</sub> for each 2 ml. of 5 *N* NaOH used. Dilute to a convenient volume. Filter with the aid of kaolin if necessary.

**Separation of Tyrosine and Tryptophan.**—Pipet aliquots containing approximately 0.3 to 0.6 mg. of tyrosine into 40-ml. graduated centrifuge tubes. Add water to the 20-ml. mark. Then add 6 ml. of precipitation reagent and place the tubes in a boiling water bath for 10 minutes. Cool the solutions and add 4 ml. of 7 *N* H<sub>2</sub>SO<sub>4</sub>. Dilute to 40 ml. with water and add 10 to 20 mg. of diatomaceous earth (Celite, Johns-Manville). Mix and centrifuge for 5 minutes. Pour the filtrates into Evelyn reading tubes. Wash the precipitates with 10 ml. of washing reagent. Centrifuge and discard the washing.

**Determination of Tyrosine.**—Add 1 ml. of 0.8% NaNO<sub>2</sub> to each tube. Mix and read after 10 minutes. Read the color against water or an hydrolyzate-reagent blank with the NaNO<sub>2</sub> omitted. Use a 520-m $\mu$  filter. Prepare a calibration curve over the range of 0.15 to 0.80 mg. of tyrosine.

**Determination of Tryptophan.**—Suspend the washed tryptophan mercury precipitate in 10 ml. of color reagent (HgSO<sub>4</sub>-HgCl<sub>2</sub>) and place the centrifuge tube in a 50° to 55°C. water bath for 15 minutes. Centrifuge. Pour the supernatant solution into an Evelyn reading tube. Wash the precipitate with 10 ml. of color reagent and, after centrifuging, add the clear liquid to the reading tube. Add 4 ml. of water. Put the reading tube in the photoelectric colorimeter and set the galvanometer to the zero point. Then add 1 ml. of 3.45% NaNO<sub>2</sub>, mix the solution by inverting and note the maximum galvanometer deflection or reading at exactly 30 seconds. Use a 420-m $\mu$  filter. In this way each tube is read against its own hydrolyzate reagent blank. The color fades quickly after the addition of NaNO<sub>2</sub>.

#### PHENYLALANINE<sup>5</sup>

**Procedure.**—Transfer aliquots of the hydrolyzate containing approximately 0.75 mg. of phenylalanine and an equal number containing twice this amount into eight 30-cm. porcelain evaporating dishes. Evaporate to dryness on the steam bath, cool, and nitrate for 20 minutes on the steam bath with 2 ml. of 20% wt./vol. KNO<sub>3</sub> in concentrated H<sub>2</sub>SO<sub>4</sub>. When the nitration is complete, pour the solutions into 25-ml. stoppered graduated cylinders. The final volume of each should not be over 12 ml. Cool to 0°C., and add 2.5 ml. of 30% wt./vol. NH<sub>2</sub>OH·HCl to three of the graduates of each set. The fourth is used as the blank. Cool in ice. Dilute with cold concentrated NH<sub>4</sub>OH to the 25-ml. mark. Swirl while adding NH<sub>4</sub>OH. Careful! Mix and allow the color to develop at room temperature for 45 minutes. Filter if necessary before the end of the waiting period. Read against the solution to which no NH<sub>2</sub>OH·HCl has been added. Use a 560-m $\mu$  color filter. Phenylalanine ranges from 0.5 to 2.0 mg.

#### · · · CYSTINE by the Winterstein-Folin Method<sup>5</sup>

**Reagent.** Phospho-18-tungstic Acid.<sup>52</sup>—Dissolve 32 to 33 ml. of 85% H<sub>3</sub>PO<sub>4</sub> in 150 ml. of H<sub>2</sub>O and add 100 g. of Na<sub>2</sub>WO<sub>4</sub>. Boil the solution gently for 1 hour and dilute to 500 ml. Then add 3 to 5 g. of Na<sub>2</sub>WO<sub>4</sub> and again boil for 10 to 15 minutes. Oxidize with a little bromine-water and boil to remove the excess Br<sub>2</sub>. The reagent should give a negative test with tyrosine and with urea plus NaCN.

<sup>52</sup> Folin, O., J. Biol. Chem., 106, 311-314, 1934.

**Procedure. Hydrolysis.**—Fifty to 250 mg. of protein are hydrolyzed under reflux with 25 ml. of 18% wt./vol. HCl for 5 to 7 hours or with an equal mixture of 18% wt./vol. HCl and 90% wt./vol. HCOOH for 18 hours. At the end of the hydrolysis, the solutions are evaporated to a thick sirup on the steam bath. This removes the excess acid and converts cysteine to cystine. The residues are dissolved in warm water, diluted to volume and filtered through soft, dry paper. The solutions should react negative to the nitroprusside test. Decolorize with a little carbon (Darco G-60) if necessary.

**Determination.**—Two aliquots (0.1 to 1.2 mg. of cystine) are pipetted into 50-ml. stoppered graduated cylinders. The solutions are brought to the 5-ml. mark with water. Five milliliters of saturated  $\text{NaHCO}_3$  are now added. After mixing, 2 ml. of Folin's phospho-18-tungstic acid, previously diluted with an equal volume of water, are added, followed immediately with either 1 ml. of water (for the blank) or 1 ml. of freshly prepared 10% wt./vol.  $\text{Na}_2\text{SO}_3$ . The solutions are mixed and the flasks are allowed to stand for 8 minutes. At the end of this time, the solutions are diluted to volume with water and read against the "blank" in a photoelectric colorimeter (photometer). Use a 520-m $\mu$  filter. Range 0.1 to 1.2 mg. of cystine.

#### METHIONINE by the Sullivan-McCarthy Method <sup>5</sup>

**Reagents.** Sodium Nitroprusside, 10% wt./vol.—Grind and make up in  $\text{H}_2\text{O}$  at room temperature. Keep in brown bottle in refrigerator.

**Procedure.**—Use 0.2 to 1.0 mg. of methionine in 1 to 7.5 ml. of solution and add  $\text{H}_2\text{O}$  to 7.5 ml. Then add 1.5 ml. of 5 N NaOH, 1.5 ml. of 1% wt./vol. glycine, and 0.3 ml. of Na nitroprusside. Mix after each addition. Put in  $\text{H}_2\text{O}$  bath at 37°C. to 40°C. for 15 minutes. Chill in an ice bath for 5 to 7 minutes. Then add 3.0 ml. of 6 N HCl to each tube as it is removed from the ice bath. Let the HCl run down the side of the tube and do not mix. Stopper. Place all tubes in a basket and shake together for *exactly one minute*. Let stand at room temperature for 15 minutes and read against water using a 520-m $\mu$  filter. Prepare a reagent blank at the same time. If the hydrolyzate is colored, add all reagents except the nitroprusside and read both reagent and hydrolyzate blanks against water, subtracting the two from the unknown.

#### SERINE AND THREONINE <sup>5</sup>

**Reagents.** Potassium Arsenite, 25 g./100 ml. of water or sodium arsenite, 22 g./100 ml. of water.

Sodium Hydrogen Sulfite, 2% wt./vol.

Periodic Acid, 0.5 M, 111 g./l.

Phosphate Buffer pH 7.2.—Make up as required, 30 ml. of  $\text{KH}_2\text{PO}_4$  solution (18.156 g./l.) and 70 ml. of  $\text{Na}_2\text{HPO}_4$  solution (19.536 g./l.).

Iodine.—Prepare standard 0.1 N  $\text{I}_2$ .

Starch Solution.—0.5% in 20% NaCl. Let stand overnight, filter, and store in refrigerator. Preserve with thymol.

Sodium Hydrogen Carbonate and Sodium Carbonate Saturated Solutions.

Sodium Carbonate, 5% wt./vol.

**Apparatus.**—Flow meter, concentrated  $\text{H}_2\text{SO}_4$  trap, 5% wt./vol. NaOH trap, oxidizing tube, two bisulfite tubes. Attach two or four adsorption trains in series.

**Procedure.** Oxidation of Amino Acids and Distillation of  $\text{CH}_3\text{CHO}$ .—An aliquot of the neutralized hydrolyzate containing 2 to 7 mg. of threonine and 2 to 7

mg. of serine is placed in the oxidizing tube. Water is added to 10 ml. The following reagents are added: 2 ml. of arsenite solution, 6 ml. of phosphate buffer, and 2 ml. of 0.5 M  $\text{HIO}_4$  with swirling to prevent the formation of free  $\text{I}_2$ . The pH of this solution *must* be approximately 8 after the addition of all reagents. The tubes are connected in series and the  $\text{CH}_3\text{CHO}$  is aerated for 30 minutes at a slow rate and then for 1 hour at a fairly rapid rate into 2 tubes each containing 2 ml. of 2% wt./vol.  $\text{NaHSO}_3$  and 20 ml. of water. At the end of the aeration time, the contents of the bisulfite tubes are washed quantitatively into an Erlenmeyer flask and titrated with  $\text{I}_2$  or the acetaldehyde is determined colorimetrically (cf. Alanine).

**Distillation of  $\text{HCHO}$ .**—Pour the contents of the oxidizing tube into a 100-ml. Kjeldahl flask (Folin and Wright,<sup>53</sup> micro-Kjeldahl apparatus). Add a boiling stone and water to 30 to 40 ml. Then add with swirling 3 to 4 drops of 1:3 vol./vol.  $\text{H}_2\text{SO}_4$  to blue to Congo red paper to release the bound  $\text{HCHO}$ . Free iodine is formed, therefore, an excess of arsenite solution is added, usually 1 to 2 ml. The reaction tube is connected to the condenser and the mixture is distilled to about 5 ml. The distillate is collected in a receiver containing 30 ml. of water and 4 ml. of 2% wt./vol.  $\text{NaHSO}_3$ . The contents of this receiver are titrated for serine with  $\text{I}_2$  or the formaldehyde is determined colorimetrically (cf. Glycine).

**Titration. Threonine.**—Add 2 ml. of starch solution and remove the excess bisulfite with 0.1 N  $\text{I}_2$ . Titrate to one drop beyond colorless. Then remove the blue color by adding one drop of 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ . Bring back to a very faint blue color by adding 0.002 N  $\text{I}_2$ . Release the bound bisulfite with 10 ml. of saturated  $\text{NaHCO}_3$  and titrate quickly with 0.02 N  $\text{I}_2$  until the blue color takes some time to disappear. Add 0.5 ml. of saturated  $\text{Na}_2\text{CO}_3$  and titrate until one drop produces a fairly permanent blue color. One milliliter of 0.02 N  $\text{I}_2$  = 1.19 mg. of threonine.

**Serine.**—Exactly the same method is used for the serine as for threonine except that 4 ml. of starch solution are used and the saturated  $\text{NaHCO}_3$  is replaced with 5 ml. of 5%  $\text{Na}_2\text{CO}_3$ . One milliliter of 0.02 N  $\text{I}_2$  = 1.05 mg. of serine.

### GLYCINE<sup>5</sup>

**Reagents.** Ninhydrin: 1% wt./vol. in water.

**Phosphate Buffer, pH 5.5.**—3.5 g.  $\text{K}_3\text{PO}_4$  are added to 100 ml. of a 20% wt./vol. solution of  $\text{KH}_2\text{PO}_4$ .

**Procedure.**—Add to the oxidizing flask the following reagents: 1 to 5 ml. of alanine solution (0.05 to 0.10 mg. of alanine), 2 ml. of buffer, and 2 ml. of ninhydrin solution. The solution is boiled for 45 to 50 minutes during which time the acetaldehyde is aerated into the bisulfite with a gentle stream of air. Then 2 ml. more of ninhydrin are added and the solution is gently boiled 25 minutes longer. Aeration is continued throughout. The bisulfite solution which now contains the acetaldehyde is diluted to 10 ml.

**Color Development.**—Pipet 1 ml. of bisulfite solution which contains acetaldehyde equivalent to 0.002–0.008 mg. of alanine into a reading tube. Add one drop of copper sulfate, 10 ml. of concentrated  $\text{H}_2\text{SO}_4$  (cool to room temperature), and approximately 50 mg. of *p*-hydroxydiphenyl. Stopper, mix from time to time and allow the color to develop overnight. The color is read using filter 540  $\text{m}\mu$  against water.

<sup>53</sup> Folin, O., and Wright, L. E., J. Biol. Chem., 38, 461–464, 1919.



HYDROXYPROLINE<sup>54</sup>

**Reagents.** Copper Sulfate, 0.01 *M*.

Sodium Hydroxide, 2.5 *N*.

Hydrogen Peroxide, 6% vol./vol.

Sulfuric Acid, 3.0 *N*.

*p*-Dimethylaminobenzaldehyde 5% wt./vol. of recrystallized, in 1-propanol.

**Procedure.**—Standards in duplicate: 1 ml. containing 5  $\mu$ g. of hydroxyproline, 1 ml. containing 10  $\mu$ g. of hydroxyproline, 1 ml. containing 15  $\mu$ g. of hydroxyproline. Unknown, 1 ml. of hydrolyzate.

To each test tube add 1 ml. of  $\text{CuSO}_4$ , 1 ml. of  $\text{NaOH}$ , and 1 ml. of  $\text{H}_2\text{O}_2$ . Shake intermittently for 5 minutes; then place in an 80°C. water bath for 5 minutes with vigorous shaking. Cool in ice bath and add 1 ml. of  $\text{H}_2\text{SO}_4$ . Mix. Heat in 70°C. water bath for 16 minutes; cool in water. Read using 510-m $\mu$  filter against a water blank.

Martin and Axelrod<sup>55</sup> have modified this method as follows: Use 2 ml. of hydroxyproline solution. Add 0.1 ml. of 20 *M*  $\text{FeSO}_4$  in 0.5% vol./vol.  $\text{H}_2\text{SO}_4$  to remove excess  $\text{H}_2\text{O}_2$ . Shake for 6 minutes. Mix  $\text{CuSO}_4$  and  $\text{NaOH}$  just before use. Add  $\text{H}_2\text{SO}_4$  and *p*-( $\text{CH}_3$ )<sub>2</sub> $\text{NC}_6\text{H}_4\text{CHO}$  simultaneously. Increase the concentration of  $\text{H}_2\text{SO}_4$  from 3 *N* to 4 *N*. Decrease the concentration of *p*-( $\text{CH}_3$ )<sub>2</sub> $\text{NC}_6\text{H}_4\text{CHO}$  from 5% to 4%.

## MISCELLANEOUS METHODS

Assays for amino acids employing microorganisms (microbiological methods) were very popular during the decade following 1915. However, these microbiological procedures have now been largely supplanted by the chromatographic methods given earlier in this chapter. Details of the microbiological techniques can be found in the monograph by Block.<sup>4</sup>

When a large number of routine assays are to be carried out for either arginine, histidine, lysine, or glutamic acid, advantage may be taken of the fact that specific L-amino acid decarboxylases for these four amino acids are commercially available (Worthington Biochemical Corporation, Freehold, N. J.). The quantity of carbon dioxide liberated from each amino acid is measured in any convenient fashion (cf. Gale,<sup>56</sup> Frank and DeMoss,<sup>57</sup> for directions). Because the L-amino and decarboxylases or the bacteria usually employed respond only to the L-amino acids, useful information can be gained if the same hydrolyzate is analyzed by both microbiological and chemical (including ion exchange) methods. Then the chemical method will give the total quantity of the amino acid present, whereas the microbiological or enzymatic techniques will give the amount of L-amino acid. As an initial assumption, the remainder can be considered to be the corresponding D-amino acid.

The availability of commercial gas chromatography equipment has encouraged a number of investigators to attempt to convert quantitatively the amino acids into volatile derivatives (esters, acyl esters, aldehydes, amines). When this can be accomplished, one would anticipate that gas chromatographic techniques will supplant many of the procedures now used.

<sup>54</sup> Neuman, R. E., and Logan, M. A., *J. Biol. Chem.*, **184**, 299-306, 1950.

<sup>55</sup> Martin, C. J., and Axelrod, A. E., *Proc. Soc. Exptl. Biol. Med.*, **83**, 161-162, 1953.

<sup>56</sup> Gale, E. F., *Biochem. J.*, **39**, 46-52, 1915.

<sup>57</sup> Frank, L. H., and DeMoss, R. D., *Arch. Biochem. and Biophys.*, **67**, 387-397, 1957.

## *Chapter 28*

# **BITUMINOUS SUBSTANCES, INCLUDING ASPHALTS, TARS, AND PITCHES**

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## ***PART I***

# ***EXAMINATION OF CRUDE, REFINED, AND BLENDED BITUMINOUS SUBSTANCES***

The methods ordinarily used for examining bituminous substances and their mixtures may be grouped under four headings:

- |                               |                                      |
|-------------------------------|--------------------------------------|
| (1) Physical characteristics. | (2) Thermal tests.                   |
| (3) Solubility tests.         | (4) Chemical methods of examination. |

In general, these tests may have one or more of the following objects in view:

- (a) To serve as a means of identification.
- (b) To ascertain the value of the substance for a given purpose.
- (c) To gauge its uniformity of supply.
- (d) As an aid to factory control in its preparation, refining, or blending.
- (e) As a criterion of its quality.

The most important methods of testing are given in Table 28-1.

Table 28-2 gives a list of the principal bituminous substances, together with such of their physical and chemical characteristics as will enable them to be distinguished, one from another.

TABLE 28-1

Description	For Pur- poses of Identi- fication	Adapta- bility for a Given Pur- pose	Gaug- ing the Uni- formity of Supply	Pur- poses of Factory Control	As a Crite- rion of the Qual- ity *
<i>Physical Characteristics:</i>					
Fracture . . . . .	YES †	—	—	—	—
Streak . . . . .	YES	Yes	—	—	—
Specific gravity . . . . .	YES	—	Yes	Yes	—
Viscosity . . . . .	—	YES	Yes	Yes	—
Penetration (Hardness) . . . . .	YES	YES	YES	YES	—
Ductility. . . . .	—	YES	Yes	Yes	—
<i>Thermal Tests:</i>					
Fusing or softening point . . . . .	YES	YES	YES	YES	—
Volatile matter . . . . .	Yes	YES	YES	YES	Yes
Evaporation test . . . . .	Yes	YES	Yes	Yes	Yes
Flash point . . . . .	—	YES	YES	YES	Yes
Fixed carbon . . . . .	YES	—	—	—	—
Distillation test. . . . .	Yes	YES	YES	YES	Yes
<i>Solubility Tests:</i>					
Solubility in carbon disulfide. . . . .	YES	YES	YES	—	YES
Carbenes . . . . .	Yes	—	Yes	Yes	YES
Solubility in petroleum naphtha . . . . .	YES	Yes	Yes	Yes	—
Free carbon in tars . . . . .	YES	Yes	Yes	—	—
<i>Chemical Tests:</i>					
Water . . . . .	Yes	—	—	—	YES
Oxygen in nonmineral matter . . . . .	YES	—	—	—	—
Solid paraffins . . . . .	YES	—	—	—	—
Sulfonation residue. . . . .	YES	—	—	—	—
Saponifiable matter. . . . .	YES	—	Yes	—	YES
Diazo reaction. . . . .	YES	—	—	—	—
Anthraquinone reaction. . . . .	YES	—	—	—	—

\* Purity; care exercised in its preparation; and intrinsic value.

† YES (capital letters) indicates test of greatest usefulness.

The commonly used tests for bituminous materials have been standardized by the American Society for Testing and Materials (ASTM) and are published triennially with yearly supplements.

Reference may also be made to "Standard Specifications for Highway Materials and Methods of Sampling and Testing," published by the American Association of State Highway Officials (AASHTO).

British practice in the testing of bituminous materials of coal-tar origin is contained in "Standard Methods for Testing Tar and Its Products," published by the Standardization of Tar Products Tests Committee, Oxford Road, Gomersal, nr. Leeds, England.

The sampling of bituminous materials is covered in ASTM D140-55.

## PHYSICAL CHARACTERISTICS

### FRACTURE

This is ascertained upon cleaving the specimen by subjecting it to a sharp blow and examining the cleavage surface. Only hard and "brittle" bituminous substances will yield to this test, including the hard asphalts and asphaltites. The fracture may appear either conchoidal (rounded and curved like a shell), or hackly (jagged, irregularly and rough).

### STREAK

This represents the color of the powder which is left behind on drawing a piece of the solid bituminous material across the surface of unglazed porcelain. Hard bituminous materials only will yield to this test. The streak may be classified as white (where no streak is visible), yellowish, yellowish-brown, brown, brownish-black, and black.

### SPECIFIC GRAVITY

*Hydrometer Method.*—Where speed is essential and great accuracy not required, the specific gravity of sufficiently fluid bituminous materials may be determined by a hydrometer. The scale shall be divided into 0.001 of a unit and the dimensions of the hydrometer shall conform to the following specifications:

	Dimension, mm.	Permissible Variation, mm.
Length of stem.....	125	$\pm 6$
Length of bulb.....	105	$\pm 5$
Length of scale.....	80	$\pm 4$
Diameter of stem.....	6	$\pm 0.5$
Diameter of bulb.....	22	$\pm 1$

The hydrometer cylinder used shall have a length of approximately 300 mm. and an inside diameter not less than 32 mm.

This method is standardized as ASTM D368-33.

*Pycnometer Method.*—This method is suitable for a variety of bituminous materials including road oils, road tar, asphalt cements, and soft tar pitches.

The pycnometer used shall be a glass vessel of cylindrical or conical shape ground to receive an accurately fitting glass stopper approximately 22 to 26 mm. in diameter. The stopper shall be provided with a hole approximately 1.0 to 2.0 mm. in

TABLE 28-2. SYNOPTICAL TABLE OF THE MOST IMPORTANT DISTINGUISHING CHARACTERISTICS OF BITUMINOUS SUBSTANCES

Genus	Species	Member	Specific Gravity at 77°F. (of Non-mineral Matter)	Endler Viscosity at 212°F. (100 ml.)	Penetration at 77°F.	Fusibility °F.	Fixed Carbon, % (Ash-free Base)	Soluble in Carbon Tetrachloride	Non-mineral Matter, Insol. in Carbon Tetrachloride	Mineral Ash, %	Carbonace, %	Soluble in Petroleum Naphtha, %	Oxygen in Non-mineral Matter, %	Solid Paraffins, %	Sulfonation Residue, % (in diox. 215-315°C.)	Tar Acids, %	Bioprecipitable Matter, %	Dioxane Reaction	Anthracene Reaction
Bitumens	Petroleums	Nonasphaltic . . . . .	0.75-0.80	—	Liquid	<32	1-2	95-100	0-1	0-1	0-1	95-100	0-2	10-25	50-100	0	0-2	0%	0%
		Semi-asphaltic . . . . .	0.80-0.95	—	Liquid	>32	2-8	85-100	0-1	0-1	0-1	95-100	0-3	0-10	50-95	0	0-2	0%	0%
		Asphaltic . . . . .	0.95-1.00	—	Liquid	>32	10	85-100	0-1	0-1	0-1	95-100	0-3	0-10	50-95	0	0-2	0%	0%
	Natural Waxes	Montanite . . . . .	0.85-1.00	—	5-10	140-200	2-10	65-100	0-2	0-2	0-2	75-95	0-2	50-90	50-100	0	0-2	0%	0%
		<10% mineral matter	0.95-1.12	—	0-5	170-200	1-10	65-100	0-2	0-2	0-2	75-95	0-2	50-90	50-100	0	0-2	0%	0%
Asphaltites	Natural Asphalt	>10% mineral matter	0.95-1.15	—	0-250	60-325	1-25	60-95	0-10	0-10	0-5	25-95	0-2	0-5	90-100	0	0-2	0%	0%
		Gilsonite . . . . .	1.05-1.10	—	0-3	250-350	10-20	95-100	0-1	0-1	0-1	40-60	0-2	Tr.	55-95	0	Tr.	0%	0%
		Glauconite . . . . .	1.10-1.15	—	0-3	250-350	20-30	85-100	0-1	0-1	0-1	40-60	0-2	Tr.	55-95	0	Tr.	0%	0%
		Grahamite . . . . .	1.15-1.20	—	0	350-600	30-55	45-100	0-5	Tr-50	0-50	Tr-50	0-2	Tr.	50-95	0	Tr.	0%	0%
		Diaterite . . . . .	0.90-1.05	—	fluid	Inf.	2-5	10-20	0-1	Tr-10	Tr-2	5-10	1-5	Tr.	80-90	—	Tr-15	0%	0%
Pyro-bitumens	Asphaltic Pyrobitumens	Wurtzite . . . . .	1.05-1.07	—	0-5	Inf.	5-25	5-10	0-95	Tr-10	Tr-2	Tr-2	0-2	Tr.	90-95	—	Tr.	0%	0%
		Albitrite . . . . .	1.07-1.10	—	0	Inf.	25-50	2-10	85-95	Tr-10	Tr-2	Tr-2	0-3	Tr.	90-95	—	Tr.	0%	0%
		Imperite . . . . .	1.10-1.15	—	0	Inf.	50-55	1-6	90-95	Tr-10	Tr-2	Tr-2	0-3	Tr.	90-95	—	Tr.	0%	0%
		Asphaltic pyrobituminous shales	1.50-1.75	—	0	Inf.	2-25	Tr-3	15-70	30-85	0-Tr.	0-Tr.	0-3	Tr-3	90-95	—	Tr.	0%	0%
		Peat (dry) . . . . .	0.15-1.05	—	0	Inf.	15-35	2-8	15-95	2-50	0-2	0-5	20-44	—	—	—	Tr-15	0%	0%
Pyrogenous Distillates	Nonasphaltic Pyrobitumens	Lignite (dry) . . . . .	1.00-1.25	—	0	Inf.	2-15	65-95	2-25	2-25	0-1	5-10	15-25	—	—	—	Tr-5	0%	0%
		Bituminous coal . . . . .	1.20-1.40	—	0	Inf.	35-75	1-2	75-95	2-25	0-1	0-1	3-15	—	—	—	Tr-1	0%	0%
		Anthracite coal . . . . .	1.30-1.60	—	0	Inf.	75-95	0-1	75-95	2-25	0	0	1-5	—	—	—	Tr-1	0%	0%
		Lignite and coal shales . . . . .	1.30-1.75	—	0	Inf.	20-45	0-1	15-70	20-85	0	0-1	3-15	—	—	—	Tr-2	0%	0%
		Wax tailings . . . . .	1.00-1.10	50-100	10-150	60-100	2-8	95-100	0-2	0-Tr.	0-Tr.	95-100	0-2	Tr-5	95-100	0	Tr.	0%	0%
Pyrogenous Tar	Pyrobitumen	Paraffin wax . . . . .	0.85-0.95	25-50	5-50	100-150	0-2	95-100	0-1	0-1	0	95-100	0-1	0-1	95-100	0	Tr.	0%	0%
		Carburetted water-gas tar . . . . .	1.00-1.15	25-50	—	<0-10	10-20	95-100	0-2	0-1	0-2	20-75	1-2	0-5	1-25	0	Tr-2	Yes	Yes
		Oil-gas tar (low-temperature) . . . . .	0.95-1.10	25-50	—	<0-20	10-25	95-100	0-2	0-1	0-2	20-75	1-2	0-5	20-40	0	Tr.	Yes	Yes
		Oil-gas tar (high-temperature) . . . . .	1.15-1.35	Over 50	—	30-100	15-35	70-90	0-1	0-1	0-2	25-70	1-2	Trace	Tr-10	0	Tr.	Yes	Yes
		Oil-gas tar (high-temperature) . . . . .	1.15-1.35	Over 50	—	30-100	15-35	70-90	0-1	0-1	0-2	25-70	1-2	Trace	Tr-10	0	Tr.	Yes	Yes



diameter, centrally located in reference to the vertical axis. The stopper pycnometer shall have a capacity of about 21 to 30 ml. and shall weigh not more than 4 ounces.

The clean, dry pycnometer is weighed to the nearest milligram on an analytical balance and this weight designated as *a*. Then fill the pycnometer with freshly boiled distilled water, firmly insert the stopper, and completely immerse the pycnometer for not less than 30 minutes in a beaker of freshly boiled distilled water maintained at 25°C. With the pycnometer and its contents at a temperature of 25°C., expose the top of the stopper and immediately wipe the water from the top of the stopper, so that this surface is dry and the meniscus of water in the bore is flush with the top of the stopper. Remove the pycnometer from the beaker of distilled water. The pycnometer may then be chilled to a temperature slightly below 25°C. Wipe all moisture from the outer surface of the pycnometer with a clean, dry cloth and weigh the pycnometer immediately. Designate this weight as *b*.

When determining the specific gravity of road oils or tars that flow readily, bring the material to a temperature of 25°C. and pour into the pycnometer until it is full, taking care to prevent the inclusion of air bubbles. Firmly insert the stopper and with the pycnometer and contents at 25°C., force all excess material through the opening, and carefully remove with a clean dry cloth. Weigh the pycnometer and contents and designate this weight as *c*.

Calculate the specific gravity as follows:

$$\text{Specific gravity} = \frac{c - a}{b - a}$$

When determining the specific gravity of tar and asphalt products that are too viscous for the method described above, bring a small amount of the material to a fluid condition by the gentle application of heat. When the sample is sufficiently fluid pour enough into the clean, dry, slightly warmed pycnometer to about half fill it. Take precaution to keep the material from touching the sides of the pycnometer above the final level and to prevent the inclusion of air bubbles. *Cool the pycnometer and contents to room temperature and weigh with the stopper.* Designate this weight as *c*. Fill the pycnometer with freshly boiled distilled water and firmly insert the stopper. Completely immerse the pycnometer for not less than 30 minutes in a beaker of freshly boiled distilled water maintained at 25°C. and follow the same procedure as described above in obtaining the weight of the water-filled pycnometer. Designate the final weight as *d*.

Calculate the specific gravity as follows:

$$\text{Specific gravity} = \frac{c - a}{(b - a) - (d - c)}$$

This method is standardized as ASTM D70-52.

**Displacement Method.**—This method is suitable for asphalts and tar pitches sufficiently solid to be handled in fragments. The sample is melted and poured into a pitch mold to form a ½ in. cube. Then tare the balance with a piece of fine waxed silk thread sufficiently long to reach from the hook on one of the pan supports to the straddle or rest. Attach the sample cube to the thread, so as to be suspended about 1 in. above the straddle from the hook on the pan support and weigh to the nearest 0.1 mg. Designate this weight as *a*. Weigh the sample

cube still suspended by the thread and completely immersed in freshly boiled distilled water at  $25 \pm 0.2^\circ\text{C}$ . to the nearest 0.1 mg., adhering air bubbles being first removed with a fine wire. Designate this weight as  $b$ .

Calculate the specific gravity of the material as follows:

$$\text{Specific gravity} = \frac{a}{a - b}$$

This method is standardized as ASTM D71-52.

## VISCOSITY

**Saybolt Method.**—This method, which is described in Chapter 40, is commonly used for petroleum products. For use at temperatures from  $70^\circ$  to  $210^\circ\text{F}$ ., it is standardized as ASTM D88-56, and for use from  $250^\circ$  to  $450^\circ\text{F}$ ., as ASTM E102-57.

**Engler Method.**—This method provides a procedure for determining specific viscosity of tars and their fluid products. It does not determine absolute viscosity, but is an empirical flow test. Only by conforming strictly to requirements of the method are reproducible results obtained.

Engler specific viscosity is the ratio obtained by dividing the time of flow, in seconds, of 50 ml. of material using an Engler viscosimeter at a selected temperature by a factor representing the time of flow, in seconds, for an equal volume of water at  $25^\circ\text{C}$ . The usual temperatures for determination of specific viscosity of tar materials are  $25^\circ\text{C}$ . ( $77^\circ\text{F}$ .),  $40^\circ\text{C}$ . ( $104^\circ\text{F}$ .),  $50^\circ\text{C}$ . ( $122^\circ\text{F}$ .), and  $100^\circ\text{C}$ . ( $212^\circ\text{F}$ .), and generally the temperature is so selected that the specific viscosity is not more than 45. This method is standardized as ASTM D1665-61 and AASHTO T54-60, and is performed as follows:

**Apparatus.**—The apparatus shall consist of the following:

(a) **Engler Viscosimeter.**—The Engler viscosimeter, as shown in Fig. 28-1, shall consist of the following:

(1) **Cup.**—This is a gold-plated cylindrical brass vessel of  $106.0 \pm 1.0$  mm.,  $A$ , inside diameter, closed at the top by a double-walled lid. To the rounded bottom is attached a metal-encased tapered platinum efflux tube  $20.0 \pm 0.1$  mm.,  $H$ , long with an inside diameter of  $2.90 \pm 0.02$  mm.,  $E$ , at the top and  $2.80 \pm 0.02$  mm.,  $F$ , at the bottom. The efflux tube shall project through and extend  $3.0 \pm 0.2$  mm.,  $G$ , below a jacket that surrounds the cup and shall have a bottom outside diameter, including its surrounding metal, of  $4.5 \pm 0.2$  mm.,  $I$ . Three metal measuring points, spaced equidistantly around the circumference of the cup, are fastened to the sides and extend inwardly approximately 7 mm., then turn up at a right angle and end in sharp points which are located  $52.0 \pm 0.5$  mm.,  $D$ , vertically above the lower end of the efflux tube and  $25.0 \pm 1.0$  mm.,  $C$ , above the lowest portion of the cylindrical sidewall of the cup. They serve both for indicating when the instrument is level and for measuring the charge of material, which is approximately 250 ml.

(2) **Jacket.**—The cup is surrounded by a jacket which holds water or other suitable liquid serving as a constant temperature bath. In the type illustrated, the jacket is provided with a thermometer clamp and stirring device. A tripod supports the apparatus and also carries a ring burner by means of which the bath is heated. Adjustable legs on the tripod serve to level the instrument. Other arrangements of outer baths, supports, and stirring devices are acceptable, especially when it is desired to use more than one standardized cup in a single bath.



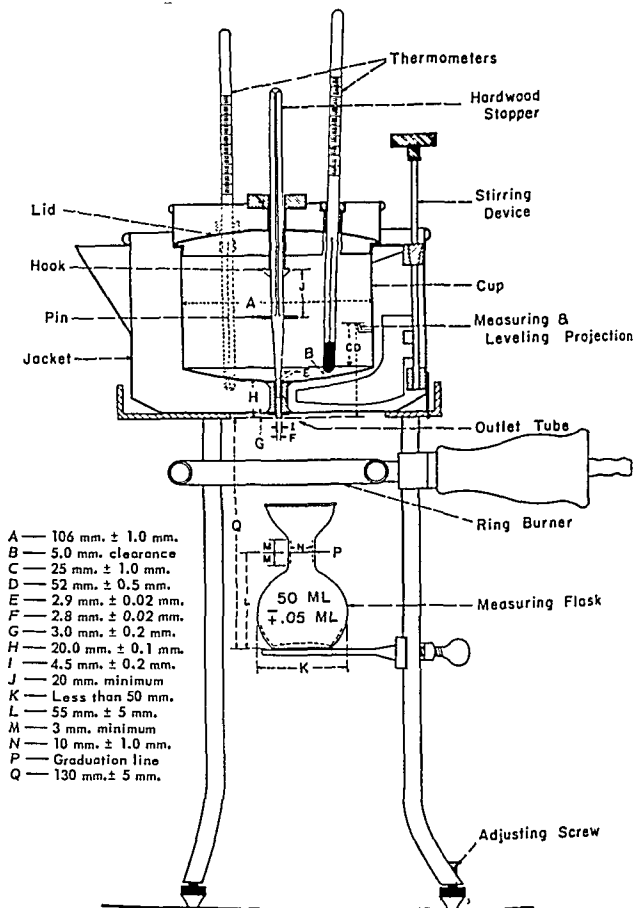
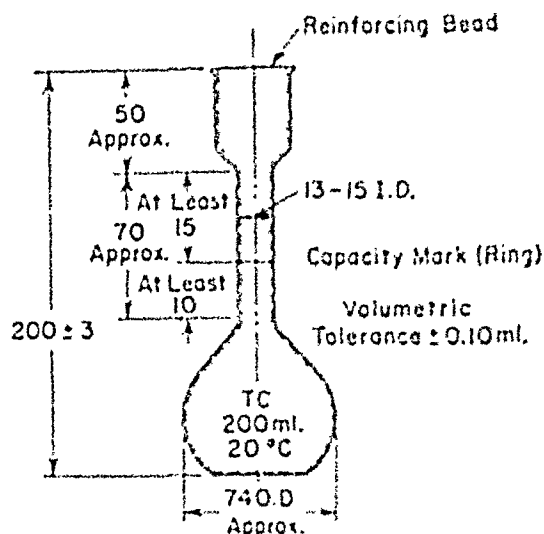


FIG. 28-1. Engler Viscosimeter.

(3) *Stopper*.—The efflux tube in the cup is closed or opened by the insertion or withdrawal of a tapered hardwood stopper which, to leave the tube open, can be suspended by its brass pin from the hook on the cover. The stopper shall be a smooth, round wooden rod, 180 mm. long and 8 mm. in diameter, with a No. 15 brass wire pin 20 mm. long inserted diametrically through the rod at a point 50 mm. from the lower end, and tapered uniformly below this pin to end in a circular plane 1.6 to 2.0 mm. in diameter. Above the pin the rod shall be planed or grooved on four sides to a depth of 1 mm. to prevent any possible restriction of air flow.

(b) *Receivers*.—Two types are required as follows:

(1) *Testing Flask*.—The receiving flask for regular testing (Fig. 28-1) shall be of glass with a capacity up to the graduation mark on its neck of  $50 \pm 0.05$  ml. at  $20^\circ\text{C}$ . At the graduation mark, the inside diameter of the neck of the flask shall be  $10 \pm 1$  mm., *N*. The cylindrical portion of the neck of the flask shall extend not less than 3 mm., *M*, above and below the graduation mark. This graduation mark shall be  $55 \pm 5$  mm., *L*, above bottom of flask (*NOTE*).



—Dimensions are in Millimeters—

FIG. 28-2. Kohlrusch Sugar Flask.

(2) *Calibration Flask*.—For standardization purposes there shall be available a Kohlrusch flask, Fig. 28-2, with top enlarged above the graduation mark and calibrated to contain  $200 \pm 0.1$  ml. at  $20^\circ\text{C}$ .

(c) *Thermometers*.—ASTM Engler viscosity thermometers  $23^\circ$ ,  $24^\circ$ , and  $25^\circ\text{C}$  as required, and conforming to the requirements for these thermometers as specified in the Specifications for ASTM Thermometers (ASTM E1).

(d) *Timer*.—Stop watch or other timing device graduated in divisions of 0.2 seconds or less, and accurate to within 0.1% when tested over a 60-minute period.

(e) *Strainer*.—No. 50 ASTM sieve conforming to the Specifications for Sieves for Testing Purposes (ASTM E11).

*Preparation of Sample*.—Stir the sample until it is homogeneous, using heat if necessary. Avoid inclusion of air bubbles, loss of volatile or other effects, which may influence the viscosity. Strain a representative portion of the sample through the strainer to eliminate particles, and proceed in accordance with Procedure (below). Strain the material directly into the viscosimeter if preferred.

*Standardization and Calibration of Viscosimeter*.—The efflux time for 200 ml. of distilled water at  $20.0^\circ\text{C}$ . with an acceptable Engler viscosimeter shall be between 50.0 and 52.0 seconds. Determine this time and the factor representing the efflux time for 50.0 ml. of water at  $25.0^\circ\text{C}$ ., as described in the following paragraphs (a) to (f):

(a) Clean the inner vessel and efflux tube of the viscosimeter with appropriate solvents, and finish by washing several times with pure methyl or 95% ethyl alcohol and rinsing several times with distilled water (*NOTE*).

**NOTE.**—In cleaning the viscosimeter take particular precautions to avoid injury to the efflux tube and measuring points. Use only a soft cloth in the cup, and soft tissue in the efflux tube. Avoid wires or similar substances and corrosive liquids. To prevent an air seal, keep the lid and lip of the cup clean at all times. After a viscosimeter has been used with bituminous materials, pay particular attention to cleaning the metal surrounding the bottom end of the efflux tube. Failure to do this may cause erratic and erroneous results.

(b) Immediately after cleaning the viscosimeter, close the efflux tube with a stopper which has never been in contact with tar, oil, or similar materials. Fill the outer bath with water at slightly below or above 20°C. as found necessary to maintain the inner temperature at 20°C. Fill the inner vessel approximately to the top of the fixed gauge points with freshly boiled distilled water at 20.0°C. Level the instrument so the tips of the gauge points lie in a plane parallel to the surface of the water, and add or remove water with a pipet until its surface is even with the extreme tips of all gauge points. Place the lid and thermometer in position and maintain the inner temperature at 20.0°C. for at least 3 minutes with frequent stirring; agitate the contents of the inner cup by holding the stopper firmly and rotating the cover back and forth and around, occasionally stirring the outer bath. Dry the bottom of the efflux tube and the area surrounding it by wiping. Carefully lift the stopper until water runs into and completely fills the efflux tube, and adjust until a hemispherical drop about 4.5 mm. in diameter hangs from and covers the lower end of the tube. Then allow to stand without agitation for 1 minute.

(c) Place a dry calibration flask  $210 \pm 10$  mm. below the discharge end, and adjust it so the flow will strike the narrow portion of the neck of the flask near or slightly below the calibration line. Start the timer and simultaneously withdraw the stopper, suspending it by the lid hook. Determine the time, in seconds, for flow of 200 ml. Repeat this determination, starting the flow under conditions described above until at least three successive determinations, varying not more than 0.2 second, are obtained. If the results obtained from three or more tests do not check within 0.2 seconds, clean the viscosimeter again and make additional trials, until three or more results agree within 0.2 second.

(d) Make another series of determinations as above, starting with the instrument freshly washed with alcohol, then with distilled water and refilled as before. The average results from the second series shall agree with the average from the first series within 0.2 second. Take the efflux time for 200 ml. at 20.0°C. as the mean of the averages of at least two series of determinations agreeing within 0.2 second. This time for an acceptable viscosimeter shall be between 50.0 and 52.0 seconds.

(e) Make additional runs as necessary, beginning with a newly cleaned viscosimeter until two successive series are in substantial agreement.

(f) The factor representing efflux time for 50 ml. of water at 25.0°C. has been found to be equivalent to the efflux time for 200 ml. of distilled water at 20.0°C. multiplied by 0.224.

**Procedure.**—(a) Thoroughly clean and dry the cup and outlet tube of the viscosimeter as described in the preceding section, paragraph (a), and insert the stopper. Fill the outer bath and bring it to the required temperature of test. Maintain the bath not more than 1°C. high for tests at 25°C., 40°C., or 50°C., and not more than 2° or 3°C. high for tests at 100°C.

(b) Pour the material into the cup until it exactly reaches the tops of the three

measuring points when the instrument is level. Position the 50-ml. testing flask so that the bottom of the flask is  $130 \pm 5$  mm. below the discharge end of the efflux tube, and adjust it so that the effluent will strike the narrow portion of the neck of the flask near or slightly below the calibration line.

(c) Place the lid and inner thermometer into position and maintain the bath, with frequent agitation, at such a temperature that the material in the viscosimeter cup remains at the test temperature. Maintain these conditions for 3 minutes. Check the accuracy of the temperature reading by holding the stopper firmly in position and rotating the cover at short intervals during the first 2 minutes, but do not disturb the material during the last minute. When these conditions have been met, withdraw the stopper from the efflux tube, simultaneously start the timer, and suspend the stopper by the hook on the cover. Determine the time in seconds for 50 ml. of material to flow from the viscosimeter (NOTE).

NOTE.—Once the material has started to flow through the efflux tube, do not use the ring burner, but maintain the required temperature by the addition or removal of water at suitable temperatures, or by an auxiliary burner momentarily directed at the outside cylindrical portion of the water jacket.

Calculation.—Calculate the Engler specific viscosity by dividing the time of flow for 50 ml. of material at the selected temperature by the factor, as previously determined, according to the following formula:

$$\text{Engler specific viscosity at } t^{\circ}\text{C.} = \frac{\text{sec. for flow of 50 ml. at } t}{\text{factor}}$$

where  $t$  = selected temperature of test, in degrees Centigrade.

Results should not differ from the mean by more than the following amounts:

Repeatability (one operator and apparatus).....	4%
Reproducibility (different operators and apparatus) .....	6%

**Float Test.**—This procedure is used largely for testing the viscosity or consistency of semisolid bituminous materials. The range of the test is limited, and it cannot be used with very fluid bituminous materials or with hard solids. It accordingly fills the gap between the Engler or Saybolt viscosimeter, on the one hand, and the needle penetrometer, on the other. The test may be used on material containing finely divided mineral matter as free carbon.

The procedure has been standardized as follows as ASTM D139-49.

The float (Fig. 28-3) shall be made of aluminum or aluminum alloy and shall be in accordance with the following requirements:

	Minimum	Normal	Maximum
Weight of float, g.....	37.70	37.90	38.10
Total height of float, mm.....	34.0	35.0	36.0
Height of rim above lower side of shoulder, mm.....	26.5	27.0	27.5
Thickness of shoulder, mm.....	1.3	1.4	1.5
Diameter of opening, mm.....	11.0	11.1	11.2

The collar shall be made of brass and shall be in accordance with the following requirements:

	<i>Minimum</i>	<i>Normal</i>	<i>Maximum</i>
Weight of collar, g.....	9.60	9.80	10.00
Over-all height of collar, mm.....	22.3	22.5	22.7
Inside diameter at bottom, mm.....	12.72	12.82	12.92
Inside diameter at top, mm. ....	9.65	9.70	9.75

The top of the collar shall screw up tightly against the lower side of the shoulder.

The assembled float and collar, with the collar filled flush with the bottom and weighted to a total weight of 33.2 g., shall float upon water with the rim  $8.5 \pm 1.5$

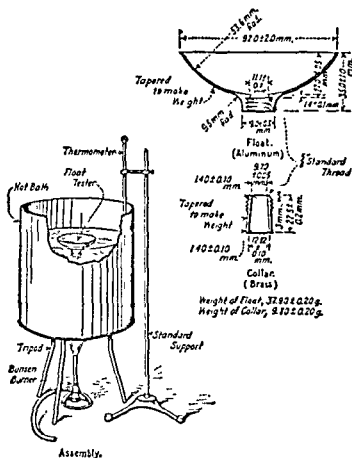


FIG. 28-3. Float Test Apparatus.

mm. above the surface of the water. Dimensions of the apparatus additional to those required above are given in Fig. 28-3. The thermometer shall be graduated in either Centigrade or Fahrenheit degrees as specified, the ranges being  $-2^{\circ}$  to  $+80^{\circ}\text{C.}$  or  $+30^{\circ}$  to  $+180^{\circ}\text{F.}$ , respectively. The diameter of the bath and the depth of water shall be at least 185 mm.

The brass collar shall be placed with the smaller end on a brass plate which has been previously amalgamated with mercury by first rubbing it with a dilute solution of mercuric chloride or nitrate, and then with mercury.

The sample shall be completely melted at the lowest possible temperature that will bring it to a sufficiently fluid condition for pouring, excepting creosote oil residues, which shall be mixed and poured at a temperature of  $100^{\circ}$  to  $125^{\circ}\text{C.}$  It

shall be stirred thoroughly until it is homogeneous and free from air bubbles. The sample shall then be poured into the collar in any convenient manner until slightly more than level with the top.

**Asphalt and Asphalt Products.**—Asphalt and asphalt products shall be cooled to room temperature for 15 to 60 minutes, placed in water maintained at  $5^{\circ}\text{C}.$  for 5 minutes, after which the surplus material shall be removed by means of a spatula, or steel knife, which has been slightly heated. The collar and plate shall then be placed in a tin cup containing ice water maintained at  $5^{\circ} \pm 1^{\circ}\text{C}.$ , and left in this bath for at least 15 minutes and not more than 30 minutes.

**Tar Products.**—Tar products shall be immediately immersed in ice water maintained at  $5^{\circ}\text{C}.$  for 5 minutes, after which the surplus material shall be removed by means of a spatula or steel knife, which has been slightly heated. The collar and plate shall be placed in a tin cup containing ice water maintained at  $5^{\circ} \pm 1^{\circ}\text{C}.$ , and then left in this bath for at least 15 minutes and not more than 30 minutes.

The bath shall then be filled with water and the water heated to the temperature at which the test is to be made. This temperature shall be accurately maintained without stirring and shall at no time throughout the test be allowed to vary more than  $0.5^{\circ}\text{C}.$  from the temperature specified. The temperature shall be determined by immersing the thermometer with the bottom of the bulb at a depth of  $40 \pm 2$  mm. below the surface.

After the material to be tested has been kept in the water bath at  $5^{\circ}\text{C}.$  for not less than 15 minutes nor more than 30 minutes, the collar with its contents shall be removed from the plate and screwed into the aluminum float and immersed in water at  $5^{\circ}\text{C}.$  for 1 minute. Any water shall then be removed from the inside of the float and the latter immediately floated in the warm bath. As the plug of material becomes warm and fluid, it is forced upward and out of the collar until the water gains entrance into the saucer and causes it to sink.

The time in seconds between placing the apparatus on the water and when the water breaks through the material shall be determined by means of a stop watch and shall be taken as a measure of the consistency of the material under examination.

**NOTE.**—Special precautions should be taken to ensure the collar fitting tightly into the float and to see that there is no seepage of water between the collar and float during the test.

## PENETRATION TEST

The penetration of a bituminous material is the distance in tenths of a millimeter that a standard needle penetrates vertically into a sample of the material under fixed conditions of temperature, load and time.

**Apparatus.**—The apparatus shall consist of the following:

**Penetration Apparatus.**—Any apparatus permitting movement of the spindle without appreciable friction and which is accurately calibrated to yield results in accordance with the description of the term penetration will be acceptable. When the needle is mounted in a ferrule, the weight of the moving spindle shall be  $47.5 \pm 0.05$  g. Regardless of the type of mounting of the needle, the total weight of the needle and spindle assembly shall be  $50.0 \pm 0.1$  g. Weights of  $50.00 \pm 0.05$  g. and  $100.00 \pm 0.05$  g. shall also be provided for total loads of 100 g. and 200 g. depending upon the conditions of test to be applied.

**Needle.**—The needle, Fig. 28-4, shall be made from fully hardened and tempered stainless steel, grade 440-C or equal, Rockwell hardness C 57 to 60. It shall be

1. For tests at 77°F. (25°C.) use an ASTM Saybolt Viscosity Thermometer 17°F. (or 17°C.) having a range of 68° to 80°F. (19° to 27°C.). The thermometer shall be immersed in the bath  $150 \pm 15$  mm.

2. For tests at 32°F. (0°C.) and 39.2°F. (4°C.) use ASTM Precision Thermometer 63°F. (or 63°C.) having a range of 18° to 89°F. (-8° to 32°C.). The thermometer shall be immersed in the bath  $150 \pm 15$  mm.

3. For tests at 115°F. (46.1°C.) use ASTM Precision Thermometer 64°F. (or 64°C.) having a range of 77° to 131°F. (25° to 55°C.). The thermometer shall be immersed in the bath  $150 \pm 15$  mm.

4. Since the accuracy of the tests results is dependent upon closely controlled temperature conditions, the thermometer used for the water bath should be accurately calibrated by the Method for Inspection, Test and Standardization of Etched-Stem Liquid-in-Glass Thermometers (ASTM E77).

**Timing Device.**—A stop watch graduated in 0.1-second intervals or an audible seconds counter is recommended for use with a hand-operated penetrometer. An automatic calibrated timing mechanism attached to the penetrometer may be used.

**Preparation of Sample.**—Heat the sample with care to prevent local overheating until it has become fluid. Then with constant stirring raise the temperature of the asphalt sample 177°F. (80°C.) to 194°F. (90°C.) or the tar-pitch sample not more than 100°F. (56°C.) above its softening point, determined in accordance with the Method of Test for Softening Point of Bituminous Materials (Ring-and-Ball Method) (ASTM D36). Avoid the inclusion of air bubbles. Then pour it into the sample container to a depth such that, when cooled to the temperature of test, the depth of the sample is at least 10 mm. greater than the depth to which the needle is expected to penetrate. Pour separate samples for each variation in test conditions.

Loosely cover each container and its contents as a protection against dust, and allow to cool in an atmosphere at a temperature not higher than 85°F. (29.5°C.) and not lower than 70°F. (21°C.) for not less than  $1\frac{1}{2}$  nor more than 2 hours when the sample is in a 6-ounce container and for not less than 1 nor more than  $1\frac{1}{2}$  hours when the sample is in a 3-ounce container. Then place the sample in the water bath maintained at the prescribed temperature of test, along with the transfer dish if used, allow it to remain for not less than  $1\frac{1}{2}$  nor more than 2 hours when the sample is in a 6-ounce container, and for not less than 1 nor more than  $1\frac{1}{2}$  hours when the sample is in a 3-ounce container.

**Test Conditions.**—Where the conditions of test are not specifically mentioned, the temperature, load, and time are understood to be 77°F. (25°C.), 100 g., 5 seconds respectively. Other conditions of temperature, load, and time may be used for special testing, such as:

Temperature	Load, g.	Time, sec.
32°F. (0°C.).....	200	60
39.2°F. (4°C.).....	200	60
115°F. (46.1°C.).....	50	5

In such cases, the specific conditions of test shall be reported.

**Procedure.**—Unless otherwise stated, place the 50-g. weight above the needle, making the total load of 100 g. for the needle and attachment. If tests are made

approximately 50.8 mm. (2 in.) in length and 1.00 to 1.02 mm. (0.0394 to 0.0402 in.) in diameter. It shall be symmetrically tapered at one end to a cone whose angle shall be within the range of  $8^{\circ} 40'$  and  $9^{\circ} 40'$  over the entire cone length from full needle diameter, and whose axis shall be coincident with the needle axis within 0.0005 in. maximum runout (total indicator reading). After tapering, the point shall be ground off to a truncated cone, the smaller base of which shall be from 0.14 to 0.16 mm. (0.0055 to 0.0063 in.) in diameter. The truncation shall be square with the needle axis within  $2^{\circ}$ , and the edge shall be sharp and free from burrs. The surface of the truncation shall be finished to a smoothness of 8 micro-inches (rms). The exposed length of the needle when mounted in the chuck of the penetration apparatus or in a ferrule shall be approximately 41.27 mm. (1½ in.). When the needle is mounted in a ferrule, the ferrule shall be a cylindrical rod,

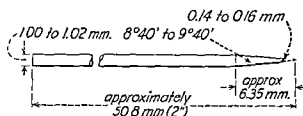


FIG. 28-4. Needle for Penetration Test  
(Courtesy ASTM.)

approximately 3.18 mm. (1¼ in.) in diameter and 38.1 mm. (1½ in.) long, made of stainless steel or brass, in which the needle shall be rigidly and coaxially mounted. The weight of the ferrule-needle assembly shall be  $2.50 \pm 0.05$  g. (A drill hole is permissible at the end of the ferrule to control weight.)

**Container.**—A container, in which the sample is tested, shall be made of metal or glass, cylindrical in shape, and have a flat bottom. The container to be used for materials having a penetration of 200 or less shall have a nominal capacity of 3 ounces; its inside dimensions shall be essentially as follows: 55 mm. (2.17 in.) in diameter and 35 mm. (1.38 in.) in depth. The container to be used for materials having a penetration greater than 200 shall have a nominal capacity of 6 ounces; its inside dimensions shall be essentially as follows: 70 mm. (2.75 in.) in diameter and 45 mm. (1.77 in.) in depth.

**NOTE.**—Containers known as tin boxes or as seamless ointment boxes may be obtained in dimensions conforming to the above requirements.

**Water Bath.**—A water bath maintained at a temperature varying not more than  $0.2^{\circ}\text{F}$ . ( $0.1^{\circ}\text{C}$ .) from the temperature of the test. The volume of water shall not be less than 10.1. The height of the bath shall be such that the sample can be immersed in the water to a depth of not less than 10 cm. (4 in.) and be supported on a perforated shelf not less than 5 cm. (2 in.) from the bottom of the bath. Do not allow the water bath to become contaminated with oil or slime. Brine may be used in the water bath for determinations at low temperatures. If penetration tests are to be made without removing the sample from the bath, a shelf strong enough to support the penetration apparatus shall be provided.

**Transfer Dish for Container.**—When used, the transfer dish for the container shall be a cylinder with a flat bottom made of glass, metal, or plastic. It shall be provided with some means which will ensure a firm bearing and prevent rocking of the container. It shall have a minimum inside diameter of 90 mm. (3.5 in.) and a minimum depth above the bottom bearing of 55 mm. (2.17 in.).

**Thermometer for Water Bath.**—The following thermometers conforming to the requirements prescribed in the specification for ASTM Thermometers (ASTM E1) are recommended:



1. For tests at 77°F. (25°C.) use an ASTM Saybolt Viscosity Thermometer 17°F. (or 17°C.) having a range of 68° to 80°F. (19° to 27°C.). The thermometer shall be immersed in the bath  $150 \pm 15$  mm.

2. For tests at 32°F. (0°C.) and 39.2°F. (4°C.) use ASTM Precision Thermometer 63°F. (or 63°C.) having a range of 18° to 89°F. (-8° to 32°C.). The thermometer shall be immersed in the bath  $150 \pm 15$  mm.

3. For tests at 115°F. (46.1°C.) use ASTM Precision Thermometer 64°F. (or 64°C.) having a range of 77° to 131°F. (25° to 55°C.). The thermometer shall be immersed in the bath  $150 \pm 15$  mm.

4. Since the accuracy of the tests results is dependent upon closely controlled temperature conditions, the thermometer used for the water bath should be accurately calibrated by the Method for Inspection, Test and Standardization of Etched-Stem Liquid-in-Glass Thermometers (ASTM E77).

**Timing Device.**—A stop watch graduated in 0.1-second intervals or an audible seconds counter is recommended for use with a hand-operated penetrometer. An automatic calibrated timing mechanism attached to the penetrometer may be used.

**Preparation of Sample.**—Heat the sample with care to prevent local overheating until it has become fluid. Then with constant stirring raise the temperature of the asphalt sample 177°F. (80°C.) to 194°F. (90°C.) or the tar-pitch sample not more than 100°F. (56°C.) above its softening point, determined in accordance with the Method of Test for Softening Point of Bituminous Materials (Ring-and-Ball Method) (ASTM D36). Avoid the inclusion of air bubbles. Then pour it into the sample container to a depth such that, when cooled to the temperature of test, the depth of the sample is at least 10 mm. greater than the depth to which the needle is expected to penetrate. Pour separate samples for each variation in test conditions.

Loosely cover each container and its contents as a protection against dust, and allow to cool in an atmosphere at a temperature not higher than 85°F. (29.5°C.) and not lower than 70°F. (21°C.) for not less than  $1\frac{1}{2}$  nor more than 2 hours when the sample is in a 6-ounce container and for not less than 1 nor more than  $1\frac{1}{2}$  hours when the sample is in a 3-ounce container. Then place the sample in the water bath maintained at the prescribed temperature of test, along with the transfer dish if used, allow it to remain for not less than  $1\frac{1}{2}$  nor more than 2 hours when the sample is in a 6-ounce container, and for not less than 1 nor more than  $1\frac{1}{2}$  hours when the sample is in a 3-ounce container.

**Test Conditions.**—Where the conditions of test are not specifically mentioned, the temperature, load, and time are understood to be 77°F. (25°C.), 100 g., 5 seconds respectively. Other conditions of temperature, load, and time may be used for special testing, such as:

Temperature	Load, g.	Time, sec.
32°F. (0°C.).....	200	60
39.2°F. (4°C.).....	200	60
115°F. (46.1°C.).....	50	5

In such cases, the specific conditions of test shall be reported.

**Procedure.**—Unless otherwise stated, place the 50-g. weight above the needle, making the total load of 100 g. for the needle and attachment. If tests are made

with the penetration apparatus mounted in the bath, place the sample container directly on the submerged stand of the penetration apparatus. If tests are made with the sample in the bath and the penetration apparatus outside the bath, place the container on the shelf provided in the bath. In the above procedures the container shall be kept completely submerged during the entire test. If tests are made using the transfer dish with the penetration apparatus outside the bath, place the sample in a dish filled with water from the bath to a depth to cover completely the sample container. Then place the transfer dish containing the sample on the stand of the penetration apparatus and penetrate immediately. In each case, adjust the needle loaded with the specified weight to just make contact with the surface of the sample. Accomplish this by making contact of the actual needle point with its image reflected by the surface of the sample from a properly placed source of light (NOTE). Either note the reading of the dial or bring the pointer to zero. Then quickly release the needle for the specified period of time and adjust the instrument to measure the distance penetrated. Observe the sample container as the needle is applied, and if any movement of the container is noted, ignore the result.

NOTE—The positioning of the needle can be materially aided by using an illuminated methyl methacrylate tube.

Make at least three penetrations at points on the surface of the sample not less than 1 cm. ( $\frac{3}{8}$  in.) from the side of the container and not less than 1 cm. ( $\frac{3}{8}$  in.) apart. If the transfer dish is used, return the dish and sample to the water bath after each penetration. Before each test, clean the needle with a clean cloth moistened with carbon tetrachloride to remove all adhering bitumen, and then wipe with a clean dry cloth. For penetration values greater than 225, use at least three needles, leaving them in the sample until completion of the penetrations.

Report to the nearest whole unit the average of at least three penetrations whose values do not differ by more than the amount shown below:

	Penetration			
	0 to 49	50 to 149	150 to 249	250 or over
Maximum difference between highest and lowest determinations.....	2	4	6	8

## DUCTILITY

This test has been standardized as follows as ASTM D113-44:

The ductility of a bituminous material is measured by the distance to which it will elongate before breaking when two ends of a briquet of the material of the form described, are pulled apart at a specified speed and at a specified temperature. Unless otherwise specified, the test shall be made at a temperature of  $25^{\circ} \pm 0.5^{\circ}\text{C}$ . ( $77^{\circ} \pm 0.9^{\circ}\text{F}$ .) and with a speed of 5 cm. per minute ( $\pm 5.0\%$ ).

The mold shall be similar in design to that shown in Fig. 28-5. Dimensions shall be as given with the permissible variations indicated. The mold shall be made of brass, the ends, *b* and *b'*, being known as clips, and the parts, *a* and *a'* as sides of the mold. The dimensions of the mold shall be such that, when properly assembled, a briquet will be formed having the following dimensions:

Total length, cm.....	7.45-7.55
Distance between clips, cm.....	2.97-3.03
Width at mouth of clip, cm.....	1.98-2.02
Width at minimum cross-section (halfway between clips), cm.....	0.99-1.01
Thickness throughout, cm.....	0.99-1.01

The water bath shall be maintained at the specified test temperature varying not more than 0.1°C. (0.18°F.) from this temperature. The volume of water shall be not less than 10 l. and the sample shall be immersed to a depth of not less than 10 cm. and shall be supported on a perforated shell not less than 5 cm. from the bottom of the bath.

For pulling the briquet of bituminous material apart, any apparatus may be

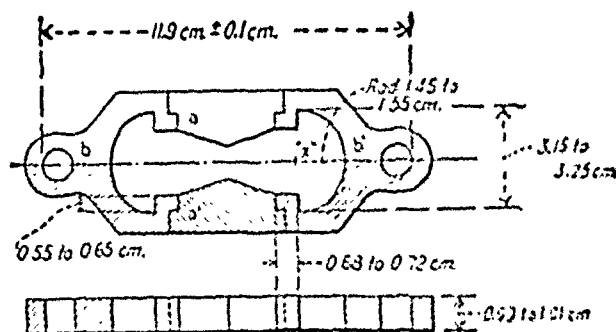


FIG. 28-5. Mold for Ductility Test Specimens. The opening in the end of each clip, as indicated by "x," shall be half an ellipse having a transverse axis of 3.2 cm.  $\pm$  0.05 cm. and half of the longitudinal axis shall be 1.15 to 1.55 cm.

used that is so constructed that the briquet will be continuously immersed in water as specified, while the two clips are pulled apart at a uniform speed, as specified, without undue vibration.

The bituminous material to be tested shall be completely melted until thoroughly fluid by heating it in an oil bath maintained at the minimum temperature needed to liquefy the sample properly. It shall then be strained through a No. 50 sieve and, after a thorough stirring, poured into the mold. The mold shall be assembled on a brass plate and, so as to prevent the material under test from sticking, the surface of the plate and interior surfaces of the sides *aa'* of the mold shall be thoroughly amalgamated (NOTE). The plate upon which the mold is placed

NOTE.—The amalgamation may best be effected by immersing the clean mold in a solution of mercury bisulfate containing free metallic mercury, and so as to come in contact with the latter. Instead of mercury, the metal mold, preferably of stainless steel, may be moistened with glycerol.

shall be perfectly flat and level so that the bottom surface of the mold will touch it throughout. In filling the mold, care shall be taken not to disarrange the parts and thus distort the briquet. In filling, the material shall be poured in a thin stream back and forth from end to end of the mold until it is more than level full. It shall be left to cool to room temperature and then placed in the water bath maintained at the specified temperature of test for 30 to 40 minutes, after which the excess bitumen shall be cut off by means of a hot straight-edged putty knife or spatula so that the mold shall be just level full.

NOTE.—When paving asphalt cements are being tested, the oil bath shall be maintained at a temperature of from 125° to 150°C. (257° to 302°F.).

The brass plate and mold, with briquet, shall then be placed in the water bath and kept at the specified temperature for 85 to 95 minutes, when the briquet shall be removed from the plate, the side pieces detached, and the briquet immediately tested. The rings at each end of the clips shall be attached to the pins or hooks in the ductility machine and the two clips pulled apart at a uniform speed as specified until the briquet ruptures. A variation of  $\pm 5\%$  from the speed specified will be allowed. The distance through which the clips have been pulled to produce rupture shall then be measured in centimeters. While the test is being made, the water in the tank of the ductility machine shall cover the sample both above and below it by at least 2.5 cm. and shall be kept continuously at the temperature specified within  $\pm 0.5^\circ\text{C}$ . ( $\pm 0.9^\circ\text{F}$ .).

A normal test is one in which the material between the two clips pulls out to a point or thread until rupture occurs at the point where the thread has practically no cross-sectional area. The average of three normal tests shall be taken and reported as the ductility of the sample.

If the bituminous material comes in contact with the surface of the water or the bottom of the bath, the test shall not be considered normal.

NOTE.—When the specific gravity of the bituminous material to be tested is below 0.98 or above 1.01, the specific gravity of the water bath in the ductility machine shall be made the same as the material to be tested by the addition of either methyl alcohol or sodium chloride.

If a normal test is not obtainable on three successive tests, the ductility shall be reported as being unobtainable under the conditions of the test.

## THERMAL TESTS

### FUSING OR SOFTENING-POINT

*Ring-and-Ball Method.*—This has been standardized as follows as ASTM D36-26:

The softening of bituminous materials generally takes place at no definite moment or temperature. As the temperature rises, they gradually and imperceptibly change from a brittle or exceedingly thick and slow-flowing material to a softer and less viscous liquid. For this reason the determination of the softening point must be made by a fixed, arbitrary, and closely defined method if the results obtained are to be comparable.

*Apparatus.*—The apparatus shall consist of the following:

(a) A brass ring 15.875 mm. ( $\frac{5}{8}$  in.) in inside diameter and 6.35 mm. ( $\frac{1}{4}$  in.) deep; thickness of wall, 2.38 mm. ( $\frac{3}{32}$  in.); permissible variation on inside diameter and thickness of ring 0.25 mm. (0.01 in.). This ring shall be attached in a convenient manner to a No. 13 B. & S. gauge brass wire (diameter 1.83 mm. = 0.072 in.). See Fig. 28-6.

(b) A steel ball 9.53 mm. ( $\frac{3}{8}$  in.) in diameter weighing between 3.45 and 3.55 g.

(c) A glass vessel, capable of being heated, not less than 8.5 cm. (3.34 in.) in diameter and measuring 10.5 cm. (4.13 in.) in depth from the bottom of the flare. (A 600-ml. beaker, low form, meets this requirement.)

*Procedure.*—The sample shall be melted at the lowest possible temperature to avoid loss of volatile constituents and stirred thoroughly, avoiding incorporating

air bubbles in the mass, and then poured into the ring so as to leave an excess on cooling. The ring, while being filled, should rest on a brass plate which has been amalgamated to prevent the bituminous material from adhering to it. After cooling for 1 hour, the excess material shall be cut off cleanly with a slightly heated knife.

*For Substances Fusing at 80°C. (176°F.) or Below.*—Use a thermometer which shall be graduated in either Centigrade or Fahrenheit degrees as may be specified, the ranges being  $-2^{\circ}$  to  $+80^{\circ}\text{C.}$ , or  $30^{\circ}$  to  $180^{\circ}\text{F.}$ , respectively (ASTM 15°C. or

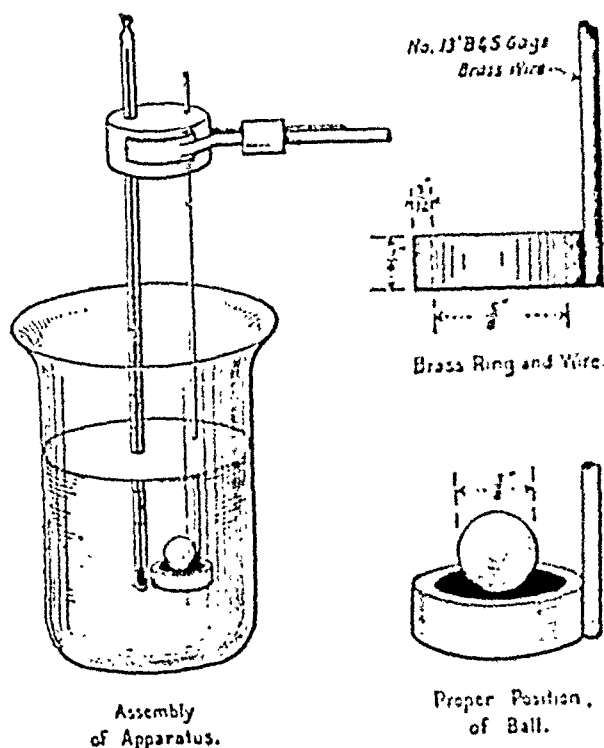


FIG. 28-6. Apparatus for Ring-and-Ball Method.

15°F.). Fill the glass vessel to a depth of substantially 8.25 cm. (3.25 in.) with freshly boiled, distilled water at 5°C. (41°F.). Suspend the ring containing the sample in the water so that the lower surface of the filled ring is exactly 2.54 cm. (1 in.) above the bottom of the glass vessel and its upper surface is 5.08 cm. (2 in.) below the surface of water. Place the ball in the water but not on the specimen. Suspend the thermometer so that the bottom of the bulb is level with the bottom of the ring and within 0.635 cm. (1/4 in.), but not touching the ring. Maintain the temperature of the water at 5°C. (41°F.) for 15 minutes. With suitable forceps, place the ball in the center of the upper surface of the bitumen in the ring, thus completing the assembly as in Fig. 28-5. Apply the heat in such a manner that the temperature of the water is raised 5°C. (9°F.) each minute. The temperature recorded by the thermometer at the instant the bituminous material touches the bottom of the glass vessel shall be reported as the softening point. No correction shall be made for emergent stem. The rate of rise of temperature shall be uniform and shall not be averaged over the period of the test. The maximum permissible variation for any minute period after the first three shall be  $\pm 0.5^{\circ}\text{C.}$

(0.9°F.). All tests in which the rate of rise in temperature exceeds these limits shall be rejected.

*For Substances Fusing Above 80°C. (176°F.).*—The thermometer shall be graduated in either Centigrade or Fahrenheit degrees as specified, the ranges being 30° to 160°C., or 85° to 320°F., respectively (ASTM 16°C. or 16°F.). The same method as given above shall be employed, except that U.S.P. glycerin shall be used instead of water, and the starting point of the glycerin bath shall be 32°C. (89.6°F.). The bath shall be brought to this temperature and thoroughly agitated, then the apparatus and specimens shall be placed in the bath which shall be maintained under agitation at the starting temperature for 15 minutes, after which the assembly shall be completed by placing the ball on the center of the specimen and the test carried on as above. In applying the heat, the ring apparatus shall be placed off the center of the container and the burner placed midway between the center and edge of the beaker away from the specimen.

Rigid adherence to the prescribed rate of heating is absolutely essential in order to secure accuracy of results. A sheet of paper placed on the bottom of the glass vessel and conveniently weighted will prevent the bituminous material from sticking to the glass vessel, thereby saving considerable time and trouble in cleaning. The limit of accuracy of the test is  $\pm 0.5^\circ\text{C}$ . (0.9°F.).

In addition to the above ring-and-ball method (ASTM D36-26), this procedure has been standardized in a modified form, covering a wider range of materials, under ASTM Designation E28-58T. The changes include the use of a shouldered ring and an agitator to ensure uniform heat distribution in the bath.

*Cube-in-water Method.*—This method is restricted to testing tar pitches, and has been standardized as follows as ASTM D61-38.

The softening of pitch takes place at no definite moment or temperature. As the temperature rises, pitch gradually and imperceptibly changes from a brittle or exceedingly thick and slow-flowing material to a softer and less viscous liquid. For this reason the determination of the softening point must be made by a fixed, arbitrary, and closely defined method if the results obtained are to be comparable.

*Apparatus.*—The apparatus shall consist of the following:

(a) A mold suitable for forming a 12.7-mm. ( $\frac{1}{2}$  in.) cube of pitch. (A recommended type is shown in Fig. 28-7).

(b) An L-shaped right-angled hook made of No. 12 B. & S. gauge copper wire (diameter 2.05 mm. = 0.0808 in.), the foot of which shall be 2.54 cm. (1 in.) long.

(c) A glass vessel, capable of being heated, not less than 8.5 cm. (3.34 in.) in diameter and measuring 10.5 cm. (4.13 in.) in depth from the bottom of the flare. (A 600-ml. beaker, Griffin low form, meets this requirement.)

(d) A thermometer graduated in either Centigrade or Fahrenheit degrees as specified, the ranges being  $-2^\circ$  to  $+80^\circ\text{C}$ . or  $+30^\circ$  to  $+180^\circ\text{F}$ ., respectively (ASTM 15°C. or 15°F.).

*Procedure.*—The pitch shall be formed into a 12.7-mm. ( $\frac{1}{2}$  in.) cube, truly shaped and with sharp edges, either by melting and pouring, or softening and pressing, into a mold. In all cases an excess of pitch shall be used and the surplus material shall be cut off cleanly with a slightly heated knife. The harder pitches specified can ordinarily be molded at room temperature, the softer pitches in water at about 4°C. (39.2°F.). If they are melted, they should first be thoroughly stirred, avoiding incorporating air bubbles in the mass, and then poured into the mold so as to leave an excess on cooling. The mold should rest on a brass plate and the surface

of the plate and the interior surfaces of the mold should be amalgamated to prevent the pitch from adhering to them.

*For Pitches Fusing Between 109.3°F. and 176°F.*—Assemble the apparatus as shown in Fig. 28-7. Fill the glass vessel to a depth of substantially 9.5 cm. (3.75 in.) with freshly boiled, distilled water at 15.5°C. (60°F.). Place the cube of pitch on

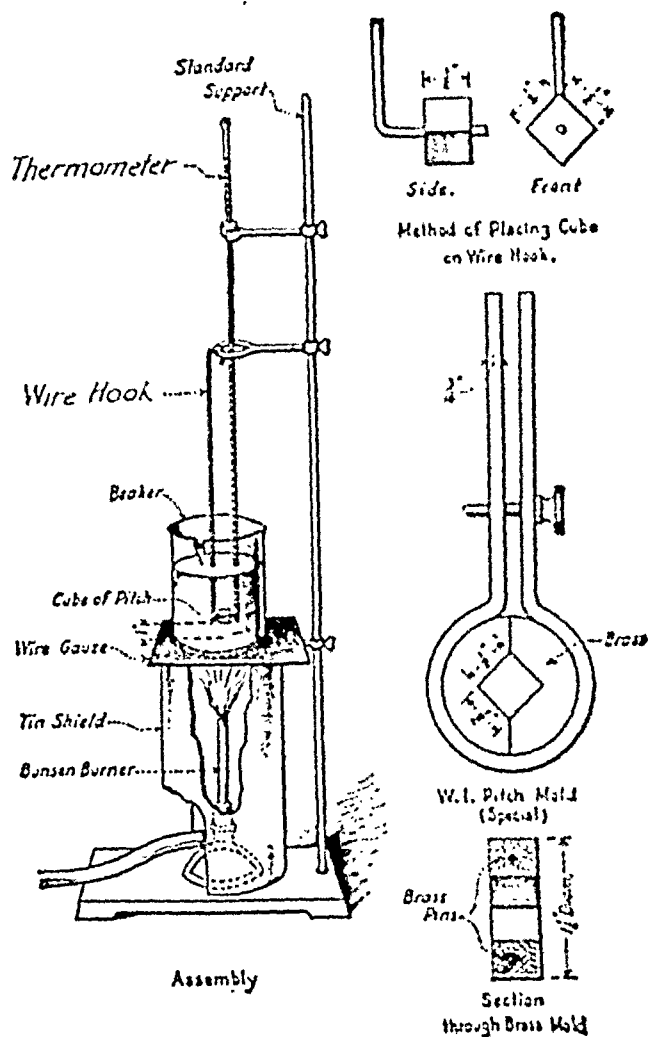


FIG. 28-7. Apparatus for Cube-in-Water Method.

the wire as shown in Fig. 28-7 and suspend it in the water so that its lower edge is exactly 2.54 cm. (1 in.) above the bottom of the glass vessel and its upper edge is 5.08 cm. (2 in.) below the surface of the water. Allow it to remain in the water for 15 minutes before applying heat. Suspend the thermometer so that the bottom of the bulb is level with the bottom edge of the cube of pitch and within 0.635 cm. (¼ in.), but not touching the cube. Apply the heat in such a manner that the temperature of the water is raised 5°C. (9°F.) each minute. The temperature recorded by the thermometer at the instant the pitch touches the bottom of the glass vessel shall be reported as the softening point. No correction shall be made for emergent stem. The rate of rise of temperature shall be uniform and shall not be averaged over the period of the test. The maximum permissible vari-

ation for any minute period after the first three shall be  $\pm 0.5^{\circ}\text{C}$ . ( $0.9^{\circ}\text{F}$ ). All tests in which the rate of rise in temperature exceeds these limits shall be rejected.

*For Pitches Fusing Below  $109.4^{\circ}\text{F}$ .*—Use the same method as given above, except that the water when placed in the glass vessel shall be at a temperature of  $4^{\circ}\text{C}$ . ( $39.2^{\circ}\text{F}$ ). The cube shall be allowed to remain 15 minutes in this water before applying the heat.

The use of freshly distilled water is essential, as otherwise air bubbles may form on the cube and retard its sinking. Rigid adherence to the prescribed rate of heating is absolutely essential in order to secure accuracy of results. A sheet of paper placed on the bottom of the glass vessel and conveniently weighted will prevent the pitch from sticking to the glass vessel, thereby saving considerable time and trouble in cleaning. The reproducibility of the test is  $1.0^{\circ}\text{C}$ . ( $1.8^{\circ}\text{F}$ ).

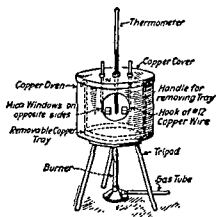


FIG. 28-8. Cube-in-Air Method for High Fusing-Point Substances.

*Cube-in-Air Method.*—This method is applicable to pitches having a softening point above  $176^{\circ}\text{F}$ . (NOTE 1). It has not been standardized by the ASTM but is commonly used in the coal-tar industry. The test is performed as follows:

*Apparatus.*—The apparatus (Fig. 28-8) shall consist of the following:

(a) Air melting-point oven, copper, with mica windows and copper tray. Arthur H. Thomas Company (A.H.T. Company) No. 1322. The copper tray shall be supported by the hooks provided, which shall give a clearance of about  $\frac{3}{16}$  in. between the bottom of the oven and the tray.

(b) Tripod. The oven shall be mounted on a suitable tripod of such size that it supports the oven at the outer edge only, leaving the bottom exposed directly to the heat of the burner.

(c) Shield, thin sheet iron, with mica windows. A.H.T. Company No. 1323.

(d) Burner, similar to A.H.T. Company No. 2583. It shall be provided with a suitable chimney, A.H.T. Company No. 2633. For electric heat a 500-watt, 115-volt ring heater, o.d.  $4\frac{1}{2}$  in., i.d.  $2\frac{1}{4}$  in. The oven is placed on the ring heater which is supported on a tripod. A variable auto transformer and a voltmeter are required to control and measure the power input.

(e) Pitch mold for forming  $\frac{1}{2}$ -in. cube. A.H.T. Company No. 1324-E.

(f) Brass Plate.

(g) Hook. An L-shaped, right-angled hook made of No. 12 B. & S. gauge copper wire; diameter 0.0808 in., the foot of which shall be 1 in. in length. A.H.T. Company No. 1324-C.

(h) Copper Cup. This shall be a copper cup  $1\frac{1}{4}$  in. in diameter and  $1\frac{1}{4}$  in. high with a capacity of about 60 ml. A slightly inclined handle  $4\frac{1}{2}$  in. long shall be attached.

(i) Thermometer,  $30^{\circ}$  to  $200^{\circ}\text{C}$ ., ASTM High Softening Point, No. 16°C.

The pitch shall be formed into a  $\frac{1}{2}$ -in. cube, truly shaped and with sharp edges, by melting and pouring into the mold. The copper cup shall be half filled with the pitch and carefully heated until the pitch is melted, stirring thoroughly and avoiding incorporation of air bubbles in the pitch. The melted pitch shall then



be poured into the mold so as to leave an excess on cooling. After cooling, the excess of material shall be cut off cleanly with a hot knife or spatula. The mold shall rest on a metal plate, and the surface of the plate and interior surfaces of the mold should be amalgamated by first rubbing them with a dilute solution of mercuric chloride or nitrate and then with mercury (see PRECAUTIONS), or thoroughly covering them with a thin film of vaseline to prevent the pitch from adhering to them (NOTE 2).

The cube shall be placed on the hook so that the foot of the hook passes through the center of two opposite faces of the cube. It shall then be suspended in the oven so that its center is level with an imaginary line running through the centers of the observation windows of the oven. The thermometer shall be supported in a vertical position so that the bottom of the bulb is level with the bottom edge of the cube. All cubes and the apparatus shall be at room temperature when heating is begun (NOTE 3).

NOTE 1.—This method of test shall be used only with pitches having a melting point, cube-in-water, over 80°C. (176°F.). In general, with pitches of this melting point, the cube-in-air melting point is 6.7°C. (12°F.) lower than the cube-in-water melting point. Results of melting point tests must always be reported in terms of the method by which the test is made.

NOTE 2.—In melting samples of pitch having a softening point above 85°C. (185°F.), at least 40 g. of the sample shall be melted for the preparation of specimens. The sample shall not be heated above the temperature necessary to pour the material readily without inclusion of air bubbles, and precautions shall be taken to prevent local overheating. If foam forms on the melted pitch, it shall be permitted to separate into a distinct layer, then removed so that the specimens may be poured from pitch substantially free from foam.

NOTE 3.—With pitches having melting points in excess of 160°C. (320°F.), it is permissible to place the cube on the hook at a temperature not above 70°C. (158°F.), and to start heating with the oven at a similar temperature.

Heat shall be applied in such a manner that the temperature of the oven is raised 5°C. (9°F.) each minute. This rate of rise in temperature shall be uniform and shall not be averaged over the period of the test. The maximum permissible variation for any 1-minute period in the 10 minutes immediately preceding the dropping of the cube shall be  $\pm 1.0^\circ\text{C}$ . (1.8°F.). All tests in which the rate of rise in temperature exceeds these limits shall be rejected.

The temperature recorded by the thermometer at the instant the pitch drops to the bottom of the oven shall be reported as the melting point. No correction shall be made for emergent stem of the thermometer.

Precautions.—Care shall be taken to avoid noticeable evolution of vapors during the heating and melting of the pitch. If necessary, an oil or sand bath shall be used.

Not more than two cubes shall be run in the oven at the same time, and these shall be pitches with melting points not more than 5°C. (9°F.) apart. The cubes shall be close to but not touching the thermometer and equidistant from it.

Owing to possible danger to health if mercury is handled carelessly, the following rules should be observed at all times.

1. Store the mercury in a closed jug in a cool place.
2. Strictly avoid spilling any mercury.
3. Remove mercury vapors by working under a suitable hood with good ventilation.

4. Keep amalgamated brass plates and other apparatus at a temperature no higher than normal room temperature.

**Kraemer and Sarnow Method.**—In this method the pitch to be tested is placed in a short length of brass or stainless steel tubing which is attached by rubber tubing to a longer piece of glass tubing. Five grams of mercury are then placed on the pitch and the assembly is heated at a controlled rate in a water bath. The temperature at which the mercury breaks through the envelope of pitch is taken as the softening point. This method is standardized by the standardization of Tar Products Test Committee (British) as No. P.T. 2-57.

### VOLATILE MATTER

This test is used for identifying various bituminous materials. Thus in the case of asphalts, the volatilization test will often serve to identify soft native asphalts, which contain larger percentages of volatile matter than soft residual or blown petroleum asphalts. Cut-back products also carry a large percentage of volatile constituents.

The test may also be used to determine the adaptability of a bituminous substance for certain definite purposes, where it becomes necessary to heat it to high temperatures, as in the paving industry or in manufacturing bituminized roofings and floorings. It serves as a valuable adjunct for gauging the uniformity of supply and for purposes of factory control. It also furnishes an *indication* of the weatherproof properties of the material. Other things being equal, bituminous substances showing the smallest percentage of volatile matter will prove most weatherproof on exposure to the elements. It should be noted, however, that the volatility test alone must not be taken as the final criterion as to whether or not a bituminous substance is weatherproof, since other factors should also be taken into consideration. The volatility test may be regarded as an accelerated test, showing the loss of volatile constituents exclusive of water which will take place upon exposure to the weather in a relatively thin layer for a long time.

The following method has been adopted as standard in ASTM D6-39T:

This test covers the determination of the loss in weight (exclusive of water) of oil and asphaltic compounds when heated as hereinafter prescribed. The material under examination shall, therefore, first be tested for water and if water is found to be present, it shall be removed by suitable methods of dehydration before the material is subjected to the loss on heating test; or another sample shall be obtained which is free from water.

**Apparatus. Oven.**—The oven shall be rectangular in form with double walls and heated by electricity. Its interior dimensions shall be as follows: height, exclusive of space occupied by the heating element, not less than 29.21 cm. (11.5 in.); width and depth, not less than 29.85 cm. (11.75 in.). The oven shall be provided with a perforated metal circular shelf approximately 24.8 cm. (9.75 in.) in diameter. A recommended form of aluminum shelf is shown in Fig. 28-9. This shelf shall be placed in the center of the oven, with respect to all dimensions of the interior of the same, suspended by a vertical shaft and provided with mechanical means for rotating it at the rate of 5 to 6 r.p.m. One side of the oven shall be hinged and equipped to serve as a tight-fitting door which shall contain a window at least 4 in. square, with double glass, through which a thermometer, located in front of and level with the revolving shelf, may be read without opening the door.

The oven shall be adequately ventilated by convection currents of air, and for

for this purpose the oven shall be provided with openings for the entrance of air and the exit of heated air and vapors. Openings for the entrance of air in interior walls of the oven shall be symmetrically arranged in the bottom or in the side walls near the bottom and shall be placed so that incoming air will circulate around the heating elements; the openings shall have a total area of not less than 1.3 sq. cm. (0.2 sq. in.). Openings for the exit of heated air and vapors in interior walls of the oven shall be symmetrically arranged in the top or in side walls near the top and shall have a total area of not less than 1.3 sq. cm. (0.2 sq. in.) nor more than 12.9 sq. cm. (2.0 sq. in.)

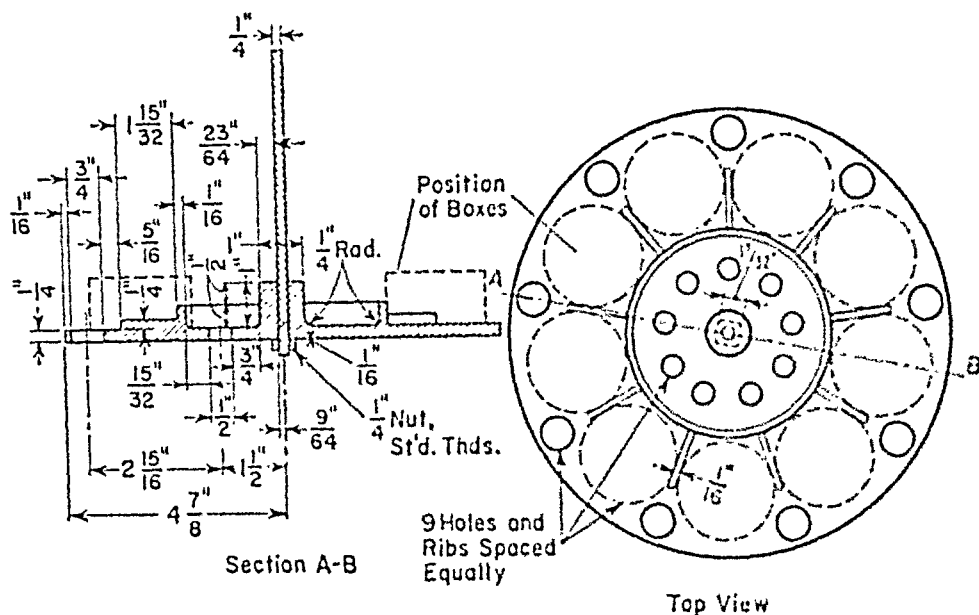


FIG. 28-9. Shelf for Volatility Oven.

**Thermometer.**—The thermometer shall be graduated in Centigrade degrees, the range being 155° to 170°C. (ASTM 13°C.).

**Container.**—The container in which the sample is to be tested shall be of metal or glass, cylindrical in shape, and shall have a flat bottom. Its inside dimensions shall be substantially as follows: diameter, 55 mm. (2.17 in.); depth, 35 mm. (1.38 in.).

NOTE.—The American Can Company's 3-ounce Gill style flat-bottom, seamless ointment box, deep pattern, fulfills these requirements.

**Procedure.**—The sample as received shall be thoroughly stirred and agitated, and warmed if necessary, to ensure a complete mixture before the portion for analysis is removed.

Fifty grams of the water-free material to be tested shall be weighed into a tared container conforming to the foregoing requirements. The oven shall be brought to a temperature of 163°C. (325°F.), and the box containing the sample placed in one of the recesses of the revolving shelf. The oven shall then be closed and the shelf rotated 5 to 6 r.p.m. during the entire test. The temperature shall be maintained at  $163^{\circ} \pm 1^{\circ}\text{C.}$  ( $325^{\circ} \pm 1.8^{\circ}\text{F.}$ ) for 5 hours after the sample has been introduced and the oven has again reached that temperature. The 5-hour period shall

start when the temperature reaches 162°C. and in no case shall the total time that a sample is in the oven be more than 5 hours and 15 minutes. The sample shall be removed from the oven, cooled, and weighed, and the loss due to volatilization calculated.

Determine temperatures by means of the specified thermometer which shall be supported from the shaft of the circular shelf in a vertical position approximately 1.9 cm. (0.75 in.) inside the periphery of the shelf, and with the bottom of the thermometer bulb 0.25 in. above the shelf.

Under ordinary circumstances a number of samples having about the same degree of volatility may be tested at the same time. Samples varying greatly in volatility should be tested separately. Where extreme accuracy is required, not more than one material should be tested at one time and duplicate samples of it should be placed simultaneously in the oven. Such duplicates shall check within the limits of accuracy given below. Results obtained on samples showing evidences of foaming during the test shall be rejected.

Up to 5% loss in weight, the results obtained may be considered as correct within 0.5. Above 5% loss in weight the numerical limit of error increases 0.01 for every 0.5% increase in loss by volatilization, as follows:

<i>Volatilization Loss, %</i>	<i>Numerical Correction</i>	<i>True Volatilization Loss, %</i>
5.0	±0.50	4.50-5.50
5.5	±0.51	4.91-6.01
6.0	±0.52	5.48-6.52
10.0	±0.60	9.40-10.60
15.0	±0.70	14.30-15.70
25.0	±0.90	24.10-25.90
40.0	±1.20	38.80-41.20

NOTE.—If additional periods of heating are desired, it is recommended that they be made in successive increments of 5 hours each. When the penetration or other characteristics of the sample after heating are required, melt the residue in the container at the lowest possible temperature and thoroughly mix by stirring, taking care to avoid incorporating air bubbles in the mass. Then bring it to the standard temperature and test as prescribed.

### TEST FOR RESIDUE OF SPECIFIED PENETRATION

This test is used principally for testing road oils, in determining the so-called asphalt content, and is carried out by evaporating the specimen under carefully controlled conditions until the residue shows a penetration of 100 at 77° F. (100 g., 5 seconds). The percentage by weight of residue is recorded and furnishes an indication of the quantity of constituents present which may be depended upon to contribute to the durability of the pavement. It will serve to differentiate between straight-distilled and cut-back products. This test has been standardized as follows as ASTM D243-36.

This method of test covers the determination of percentage of residue having a specified penetration at 100 g., 5 seconds, 25°C. (77°F.), obtained by heating a road oil or a semisolid asphalt having a penetration of more than 100, at a temperature of 249° to 260°C. (480° to 500°F.). When the penetration of the residue is not otherwise stated it shall be understood to be 100. The residue obtained is available for testing as desired.

**Apparatus.**—The apparatus shall consist of a container, heating bath, hot plate,

and thermometer, with necessary accessory apparatus. The container in which the sample is to be tested shall be a flat-bottom, cylindrical seamless tin box, 70 mm. ( $2\frac{3}{4}$  in.) in diameter and 45 mm. ( $1\frac{3}{4}$  in.) in depth.

NOTE.—The American Can Company's 6-ounce Gill style flat-bottom, seamless ointment box, deep pattern, fulfills these requirements.

**Heating Bath.**—The heating bath shall be a cast-iron air-bath permitting the immersion of the container to a depth of  $1\frac{1}{4}$  in. through an opening  $\frac{1}{8}$  in. larger in diameter than the container. It shall support the container  $\frac{1}{4}$  in. above the hot plate and with at least  $\frac{1}{4}$  in. free air space between the sides of the container and of the air bath below the opening. A suitable air bath is shown in Fig. 28-10.

**Air Bath.**—The air bath shall be heated upon a suitably mounted hot plate, heated either electrically or by means of a gas flame. The plate shall be capable of maintaining the sample continuously at the required temperature, and apparatus necessary to fulfill this requirement, such as a rheostat or gas pressure regulator, shall be provided.

**Thermometer.**—The thermometer shall conform to the following requirements. These specifications cover a special thermometer graduated to either Centigrade or Fahrenheit degrees as specified, the ranges being  $-6^{\circ}$  to  $+100^{\circ}\text{C.}$ , or  $+20^{\circ}$  to  $+760^{\circ}\text{F.}$ , respectively (ASTM  $11^{\circ}\text{C.}$  or  $11^{\circ}\text{F.}$ ). The sample as received shall be thoroughly stirred and agitated, to ensure a complete mixture before the portion for testing is removed.

**Procedure.**—One hundred grams ( $100.00 \pm 0.10$  g.) of the material to be tested shall be weighed into a tared container, which shall then be placed in the air bath in position to be heated. The thermometer shall be supported in the sample equidistant from the sides of the container and with the bottom of the bulb neither more than  $\frac{1}{4}$  in. above nor touching the bottom of the container. The bulb shall be completely immersed in the sample throughout the heating. An assembly of the apparatus is shown in Fig. 28-11.

The sample should be heated as rapidly as possible, to prevent foaming, to a temperature of  $249^{\circ}\text{C.}$  ( $480^{\circ}\text{F.}$ ) and during the evaporation, the temperature shall be maintained between  $249^{\circ}\text{C.}$  ( $480^{\circ}\text{F.}$ ) and  $260^{\circ}\text{C.}$  ( $500^{\circ}\text{F.}$ ). The sample shall be stirred with the thermometer from time to time to prevent local overheating and, to maintain a homogeneous sample, all cakes of hardened bitumen which form at the sides of the container shall be fluxed in the sample.

An experienced operator can judge approximately what percentage of residue he should obtain to secure the desired penetration. When it is supposed that

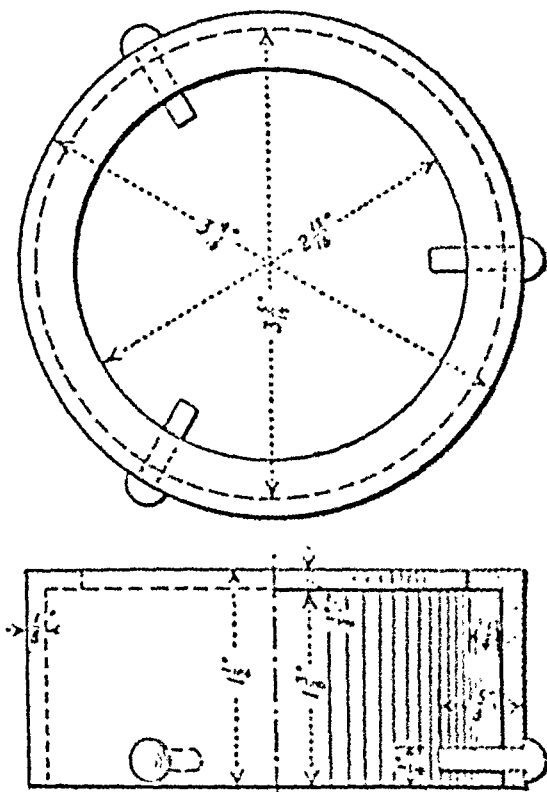


FIG. 28-10. Cast-Iron Air Bath.

the residue will show the required penetration, the bitumen on the thermometer which may be readily scraped off shall be returned to the container, which then shall be removed from the air bath, cooled and weighed. The penetration of the residue shall then be determined with the exception that the 6-ounce container in which the evaporation has been conducted, shall be used instead of the 3-ounce container specified in the test for "penetration."

It frequently is necessary to make several trials before a residue of the required penetration is obtained. If it is determined to be greater than that required, all water shall be removed from the container and the surface of the sample, and the heating and determination of penetration may be repeated as before. Ordinarily a residue shall be considered as satisfactorily obtained when its penetration is within 15 of that desired, and its percentage by weight of the original sample shall be calculated. When it is necessary to determine more precisely the percentage of residue having the specified penetration, such a percentage shall be computed by interpolation between percentages of two residues, one having a penetration greater and one having a penetration lower than that specified. The percentage shall be reported as:

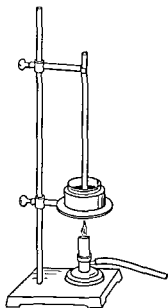


FIG. 28-11. Assembly of Apparatus for Evaporation Test.

Percentage of residue of..... penetration (determined ..... ) stating, first, the specified penetration, and second, the penetration actually determined for the sample tested or calculated by interpolation.

Certain types of road oil will readily form rings of hard asphalt at the side of the container. Great care should be taken that this material be completely fluxed in the sample before the penetration of the residue is determined. Duplicate determinations should not differ by more than 1.0% with the same operator nor more than 2.5% between different laboratories.

In case it is desired to determine the residue of specified penetration with the elimination of oxidation effects, a vacuum distillation method may be used which has been standardized as ASTM D1189-61.

### FLASH POINT

A number of flash-point testers are in use, including the Pensky-Martens (ASTM D93-61), Cleveland Open Cup (ASTM D92-57), and the Tag types (ASTM D1310-59T), which are fully described in Chapter 40.

### FIXED CARBON

The same procedure may be followed as for testing Coal (Volatile Combustible Matter) as described on p. 1152.

This test which has been standardized as ASTM D271-58 involves heating 1 g. of the sample under controlled conditions at  $950 \pm 20^\circ\text{C}$ . for 7 minutes and determining the loss in weight.

The Conradson carbon residue test may also be used to determine fixed carbon. This test is standardized as ASTM D189-61.

## DISTILLATION TEST

The value of this test is to ascertain the adaptability of bituminous materials for a given use, generally for road treatment; for gauging the uniformity of supply, for purposes of factory control, and, most important of all, as a criterion of the quality. This test is generally applied to tar products as an equivalent of the volatility test becomes of value in identifying the kind used (upon determining the specific gravity of the fractions distilled), as a means of distinguishing a cut-back tar from a straight-distilled tar (upon determining the specific gravity of the fractions, their viscosity, and the fusing point of the residue), and for detecting the presence of abnormal amounts of naphthalene.

This test has been standardized as follows as ASTM D20-56:

*FOR ROAD OILS (ASPHALTIC AND COAL-TAR PITCH), ETC.*

*Apparatus.*—The apparatus consists of a flask, condenser tube, shield, receivers, and thermometers as specified.

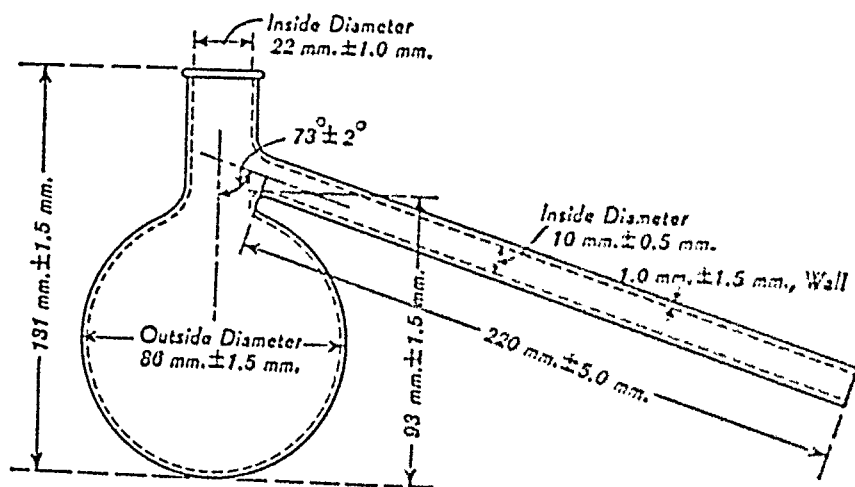


FIG. 28-12. Distillation Flask.

(a) *Flask.*—The distillation flask, Fig. 28-12, shall be a side neck distilling flask, having the following dimensions:

Diameter of bulb, outside, mm.....	86	± 1.5
Diameter of neck, inside, mm.....	22	± 1.0
Diameter of tubulature, inside, mm.....	10.0	± 0.5
Height of flask, outside, mm.....	131	± 1.5
Vertical distance bottom of bulb, outside, to horizontal tangent at tubulature inside, mm.....	93	± 1.5
Length of tubulature, mm.....	220	± 5.0
Angle of tubulature, degrees.....	73	± 2
Thickness of tubulature wall, mm.....	1.0 to 1.5	

(b) *Condenser Tube.*—The condenser tube shall be a suitable form of tapered glass tubing of the following dimensions:

Outside diameter of small end, mm.....	12.5 ± 1.5
Outside diameter of large end, mm.....	28.5 ± 3.0
Length, mm.....	360.0 ± 4.0
Length of tapered part, mm.....	100.0 ± 5.0

(c) **Shield.**—A galvanized iron shield, lined with  $\frac{1}{8}$ -in. asbestos, of the form and dimensions shown in Fig. 28-13 shall be used to protect the flask from air currents and to prevent radiation. The cover (top) may be of transite board made in two parts, or it may be of galvanized iron lined with  $\frac{1}{8}$ -in. asbestos.

(d) **Receiver.**—The distillates shall be collected in tared Erlenmeyer flasks having a capacity of 50 to 100 ml.

(e) **Thermometer.**—The thermometer shall be graduated in either Centigrade or Fahrenheit degrees as specified, the range being from  $0^{\circ}$  to  $400^{\circ}\text{C}$ . or  $30^{\circ}$  to  $760^{\circ}\text{F}$ ., respectively (ASTM  $8^{\circ}\text{C}$ . or  $8^{\circ}\text{F}$ .).

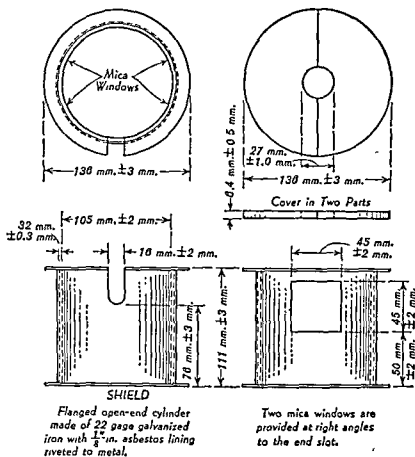


FIG. 28-13. Shield.

**Procedure.**—The sample, as received, shall be thoroughly stirred and agitated, warming if necessary, to ensure a complete mixture before the portion for analysis is removed.

The material may be tested for distillation without dehydration, if water is present not to exceed 2.0%. If water is present in excess of 2.0%, the bituminous material shall be dehydrated before testing, by distilling 500 ml. in an 800-ml. copper still provided with a water-cooled condenser, the distillate being caught in a separatory funnel. When all the water has been expelled, the distillate is allowed to settle, the water drawn off and the oils returned to the residue in the still after the contents have cooled below  $212^{\circ}\text{F}$ .

The flask shall be supported on a tripod or rings over two sheets of 20 mesh



gauze, 150 mm. square, as shown in Fig. 28-14. It shall be connected to the condenser tube by a tight cork joint. The thermometer shall be inserted through a cork in the neck with the top of the bulb level with the lowest point of juncture of the tubulature and neck of the flask.

The axis of the flask through the neck shall be vertical.

The distance from the bulb of the thermometer to the outlet end of the condenser tube shall be not more than 540 nor less than 500 mm. The burner should be protected from drafts by a suitable shield or chimney.

One hundred grams ( $100 \pm 0.1$  g.) of the sample shall be weighed into the flask, the apparatus assembled and heat applied so that the first drop comes over in from 5 to 15 minutes. The distillation shall be conducted at the rate of between 50 and 70 drops per minute and the distillate collected in weighed receivers.

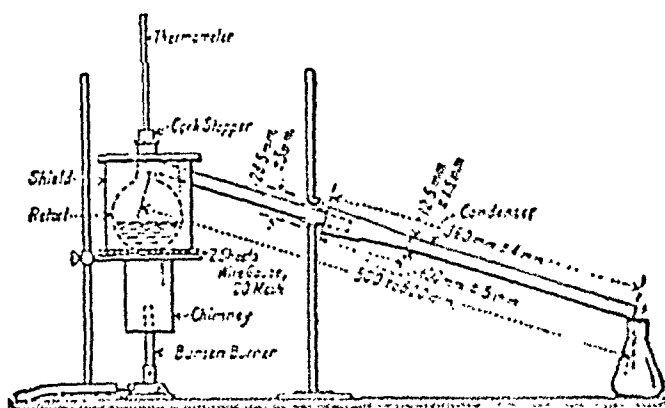


FIG. 28-14. Distillation Apparatus Assembly for Road Oils.

The condenser tube shall be warmed whenever necessary to prevent accumulation of solid distillates. The fractions shall be collected at the points designated by the specifications. The receivers shall be changed when the thermometer indicates the maximum temperature for each fraction. When the maximum specified temperature of the test is indicated by the thermometer, the flame shall be removed and any oil which has condensed in the condenser tube shall be drained into the last fraction.

The residue shall remain in the flask, with the cork and thermometer in position, until no vapors are visible and it shall then be weighed. If tests of the residue are required, the flask shall then be inclined so that the residue will flow around the sides, thus collecting any condensed vapors that may be on the sides of the flask, after which the residue shall be poured into a suitable receptacle and covered. If the residue becomes so cool that it cannot be poured readily from the flask, it shall be reheated to a temperature not exceeding  $150^{\circ}\text{C}$ . by holding the bulb of the flask in a suitable bath and not by the application of flame. For weighing the receivers and fractions, a balance accurate to at least 0.05 g. shall be used.

During the progress of the distillation the thermometer shall remain in its original position. No correction shall be made for the emergent stem of the thermometer, but if the altitude at which the distillation is made exceeds 1000 ft. above sea level, adjust the temperatures in accordance with Table 28-3. The re-

TABLE 28-3

Elevation Above Sea Level, ft.	Fractionation Temperatures for Various Altitudes, °C.					
	170	200	235	270	300	355
0						
1000	169	198	233	268	298	353
1500	168	198	232	267	297	352
2000	167	197	231	266	296	351
2500	167	196	230	265	295	350
3000	166	195	230	264	294	349
3500	165	195	229	263	293	348
4000	165	194	228	263	292	347
4500	164	193	227	262	291	346
5000	164	192	226	261	290	345
5500	163	192	225	260	289	344
6000	162	191	225	260	288	343

sults of the distillation test shall be reported in percentages by weight of water-free material.

#### FOR CUT-BACK ASPHALTIC PRODUCTS

In testing cut-back asphaltic products, the foregoing method is modified in the following particulars and is standardized as ASTM D402-55.

**Apparatus. Condenser.**—The condenser shall consist of a 250-mm. standard glass-jacketed condenser (Fig. 28-15).

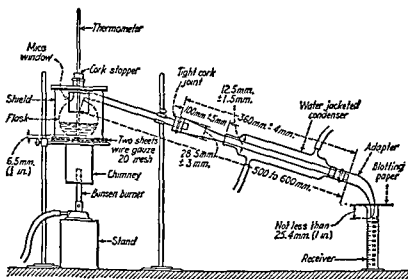


FIG. 28-15. Distillation Apparatus Assembly for Cut-Back Asphaltic Products.

The following dimensions are recommended:

Length of jacket, excluding necks, mm.....	250	$\pm 5$
Outside diameter of expanded end of condenser tube, mm.....	23	$\pm 1$
Outside diameter of condenser tube proper, mm.....	12.5	$\pm 0.5$
Length of condenser tube, mm.....	400	$\pm 25$
Length of expanded end of tube, mm.....	75	$\pm 1$

**Adapter.**—The adapter shall be of the curved design of heavy wall (1 mm.) and reinforced top glass, with an angle of approximately  $105^\circ$ , and with a diameter at the large end of approximately 18 mm., and the small end not less than 5 mm. The outlet end shall be ground to an angle of  $45^\circ \pm 5^\circ$  with the inside vertical.

**Flask.**—The flask shall be a 500-ml. side-neck distillation flask having the following dimensions:

Diameter of bulb, outside, mm.....	102	$\pm 2.0$
Diameter of neck, inside, mm.....	25	$\pm 1.2$
Diameter of tubulature, inside, mm.....	10	$\pm 0.5$
Height of flask, outside, mm.....	135	$\pm 5$
Vertical distance from bottom of bulb, outside, to horizontal tangent at tubulature, inside, mm.....	105	$\pm 3$
Length of tubulature, mm.....	220	$\pm 5$
Angle of tubulature, degrees.....	75	$\pm 3$
Thickness of tubulature wall, mm.....	1.0 to 1.5	

**Iron Shield.**—A galvanized iron shield lined with  $\frac{1}{8}$ -in. asbestos and fitted with transparent covered windows of the form shown in Fig. 28-14 is used to protect the flask from air currents and to prevent radiation. The cover (top) shall be made in two parts and may be of transite board or of galvanized iron lined with  $\frac{1}{8}$ -in. asbestos.

**Thermometer.**—The thermometer used is an ASTM partial immersion  $3^\circ\text{F.}$  or  $3^\circ\text{C.}$  having a range, respectively, of  $20^\circ$  to  $760^\circ\text{F.}$  or  $-5^\circ$  to  $400^\circ\text{C.}$

**Receivers.**—The receivers shall be graduated cylinders, of uniform diameter, with a pressed or molded base and a lipped top. The overall height shall be not less than 24.8 cm. (9 $\frac{3}{4}$  in.) nor more than 26.0 cm. (10 $\frac{1}{4}$  in.). The cylinder shall be graduated in single milliliters to contain 100 ml., and the graduated portion shall be not less than 17.78 cm. (7 in.) nor more than 20.32 cm. (8 in.) in length. Each fifth graduation shall be distinguished by a longer line, and the graduations shall be numbered from the bottom up at intervals of 10 ml. The graduations shall not be in error by more than 1 ml. at any point on the scale.

The flask shall be supported on a tripod or ring over two sheets of 20-mesh gauze, 150-mm. square as shown in Fig. 28-15. It shall be connected to the condenser tube by a tight cork joint. The thermometer shall be inserted through a cork in the neck with the bottom of the bulb  $\frac{1}{4}$  in. from the bottom of the flask. The axis of the flask through the neck shall be vertical. The distance from the neck of the flask to the outlet end of the condenser tube shall be not more than 700 nor less than 600 mm. The burner should be protected from drafts by a suitable shield or chimney.

The adapter shall be adjusted over the end of the condenser tube so as to conduct the distillate into the receiver, and the top of the receiver shall be covered closely during the distillation with a piece of blotting paper or its equivalent, which shall be cut so as to fit the adapter tightly. The adapter shall extend into the receiver at least 2.54 cm. (1 in.) but not below the 100-ml. mark. Unless the

## 984 EXAMINATION OF BITUMINOUS SUBSTANCES

laboratory air temperature is between 12.8° and 18.3°C. (55° and 65°F.) the receiver shall be immersed up to the 100-ml. mark in a transparent bath maintained between these temperatures. The condenser tube shall be clean and dry.

Two hundred milliliters (calculated from the specific gravity of the material at 15.5°C. (60°F.)) of the sample shall be weighed into the flask, the apparatus assembled and heat applied so that the first drop comes over in from 5 to 15 minutes.

The distillation shall be conducted so as to maintain the following rates:

50 to 70 drops per minute to 500°F. (260°C.)

20 to 70 drops per minute between 500°F. (260°C.) and 600°F. (316°C.)

Not more than 10 minutes should be allowed for completion of the distillation from 600°F. (316°C.) to 680°F. (360°C.), with the exception that, near the end of the distillation, the heat input shall not be so rapid as to result in a temperature in excess of 680°F. (360°C.) after the flame has been removed. Should the sample foam, the distillation rate will have to be reduced, but the normal rate shall be resumed as soon as possible. If excess foaming persists, the distillation may be more easily controlled by applying the flame near the edge of the bulb instead of at the center of same. The distillate shall be collected in the specified receivers, and the volume of distillate at all specified temperatures recorded. The volume of any separated water shall also be recorded. When the maximum specified temperature of the test is indicated by the thermometer, the flame shall be removed and the residue poured *immediately* into an 8-ounce tin box placed on its cover to prevent too rapid cooling at the bottom. Any oil which may remain in the condenser tube shall be drained into the last receiver.

As soon as no further vaporization is apparent, the residue shall be stirred to ensure homogeneity, and then poured into the necessary apparatus for the required tests. During the progress of the distillation the thermometer shall remain in its original position. No correction shall be made for the emergent stem of the thermometer. Temperatures to be observed in the distillation test shall be corrected for the effect of the altitude of the laboratory in which the test is made.

The results of the distillation test shall be reported in percentage by volume of water-free material.

For testing creosote, tar, petroleum, and mixtures of creosote with tars or petroleum used for wood preservation, the method of distillation is standardized as ASTM D246-59. This differs from ASTM D20-56 described above in that the thermometer is placed 12 to 13 mm. above the surface of the liquid in the flask and the rate of distillation is 80 to 100 drops per minute. Also, the use of electric heat is optional.

## SOLUBILITY TESTS

### SOLUBILITY IN CARBON DISULFIDE

This test is useful for purposes of identification, for ascertaining the adaptability of a bituminous substance for a given purpose, for gauging its uniformity of supply, and as a criterion of its quality (i.e., purity) and consequently its intrinsic value. Crude bituminous materials are often purchased on the basis of the percentage soluble in carbon disulfide. In the case of native asphalts, the larger the percentage soluble in carbon disulfide, the greater will be their intrinsic value.

The percentage and composition of the mineral matter will often indicate the source of the native asphalts. Asphalts derived from petroleum are substantially free from mineral constituents, and with the possible exception of the harder grades, contain little to no nonmineral matter insoluble in carbon disulfide.

With a native asphalt containing over 10% of mineral matter, it is necessary to separate the portion soluble in carbon disulfide before ascertaining its physical characteristics, fusing point, and sometimes fixed carbon, in which case the soluble constituents should be recovered as will be described.

The determination of the carbon disulfide soluble (bitumen) in a sample of bituminous material has been standardized by the ASTM under the designation D-452 and is performed as follows:

This method of test is intended for the determination of bitumen in materials containing at least 25% bitumen. Bitumen may usually be expeditiously and accurately determined by Procedure No. 1 (given subsequently). However, some bituminous materials containing finely divided mineral matter may clog the filter or the mineral residue may not be easily retained, in which case Procedure No. 2 shall be followed.

*Apparatus.*—The apparatus materials shall consist of the following:

(a) Gooch crucible, approximately 4.4 cm. in width at the top, tapering to 3.6 cm. at the bottom, with a depth of 2.5 cm.

(b) Asbestos (amphibole), Gooch grade, acid washed, in pieces not exceeding 1 cm. in length, shredded, and shaken up with water.

(c) Beakers.—One 30-ml. beaker, Griffin low form, and one 150-ml. beaker, Griffin low form.

(d) Carbon disulfide, c.p.

(e) Filtering flask.

(f) Filter tube.

(g) Diatomaceous earth filter aid.

*Preparation of Sample.*—The sample shall be representative, and if it contains more than 2% of water it shall be dehydrated in accordance with the Standard Method of Test for Water in Creosote (ASTM D370-58). If the material is hard and brittle, it may be ground, and dried at a temperature below the temperature of volatilization of the material.

*Preparation of Gooch Crucible.*—Insert the filter tube in the stopper of the filtering flask, set the Gooch crucible in the filtering tube, and connect the flask to the suction pump. Fill the crucible with some of the suspension of asbestos in water, allow it partly to settle in the crucible, and apply a light suction to draw off the water, leaving a firm mat of asbestos in the crucible. Add more suspended asbestos and repeat the process until a mat is built up which, after ignition, will weigh  $0.5 \pm 0.1$  g. (NOTE). Wash the asbestos mat thoroughly with water, dry in the oven, and ignite to a dull red heat. Cool the crucible in the desiccator, weigh, and replace it in the dry filter tube supported in the clean, dry filtering flask.

NOTE.—In the determination, the asbestos and filter aid apparently adsorb irreversibly a small amount of soluble bitumen (usually 1 to 5 mg. per gram of asbestos and filter aid). The weights of asbestos and filter aid used should, therefore, be kept within the specified limits to ensure reproducible results.

*Procedure No. 1 (Small Amount of Finely Divided Insoluble Matter Present).*—

(a) Weigh approximately 2 g. of the sample into a tared 150-ml. beaker and add 100 ml. of carbon disulfide to the beaker in small portions, with continuous

agitation, until all lumps disappear and nothing adheres to the beaker. Cover the beaker with a watch glass and set it aside for 15 minutes.

(b) Decant the carbon disulfide solution carefully through the asbestos mat in the prepared Gooch crucible, with or without light suction as may be necessary, retaining as much sediment as possible in the beaker until the solution has drained through the mat. Wash the beaker with a small amount of carbon disulfide and transfer all sediment from the beaker to the asbestos mat. Wash with carbon disulfide until the filtrate is substantially colorless, then apply strong suction to remove the remaining carbon disulfide. Remove the Gooch crucible from the tube, wash the bottom free of any bitumen, and place the crucible on top of the oven until practically all of the carbon disulfide has been driven off. Place in an oven at  $110^{\circ} \pm 10^{\circ}\text{C.}$  for at least 20 minutes. Cool in a desiccator and weigh.

(c) If insoluble matter adheres to the beaker, dry the beaker in the oven at  $110^{\circ}\text{C.}$  and weigh. Add the weight of this adherent material as a correction to the weight of the insoluble matter in the Gooch crucible.

(d) If a determination of mineral matter be required, ignite the Gooch crucible from paragraph (b) at a red heat until any black or glowing spots are burned off. Cool in a desiccator and weigh. The correction, paragraph (c), shall be added to the weight of mineral matter in the Gooch crucible. If a carbonate mineral is present, add to the ignited mineral matter a few drops of ammonium carbonate solution, dry at  $100^{\circ}\text{C.}$ , heat for a few minutes to a dull red heat, cool in a desiccator, and weigh (NOTE).

NOTE.—In the event that water-soluble salts insoluble in carbon disulfide are present, the amount of these salts may be determined in accordance with the procedure described in the 1937 Report of Committee D-4 on Road and Paving Materials (Vol. 37, Part 1).

(e) If there is any question involving the amount of mineral matter that may have passed through the filter, a correction may be determined as described in paragraph (d) of Procedure No. 2.

**Procedure No. 2 (Substantial Amount of Finely Divided Insoluble Matter Present).—**(a) Weigh approximately 2 g. of the sample into a tared 30-ml. beaker. Add about 0.5 g., weighed to the nearest 0.001 g., of freshly ignited diatomaceous earth filter aid. Cover with about 25 ml. of carbon disulfide and stir the filter aid into the liquid. Let stand, covered with a watch glass, at least 1 hour, stirring occasionally to dissolve the sample completely.

(b) Immediately before starting the filtering process, stir the filter aid into the liquid. Wet the asbestos pad in the Gooch crucible with carbon disulfide. Pour the solution from the beaker onto the Gooch pad, filling the Gooch crucible to the top. Apply light suction and, as the liquid filters through, pour the remaining contents of the 30-ml. beaker into the crucible. Wash the beaker with a small amount of carbon disulfide and transfer all sediment from the beaker to the asbestos mat. Wash with carbon disulfide until the filtrate is substantially colorless, then apply strong suction to remove the remaining carbon disulfide. Remove the crucible from the tube, wash the bottom free of any bitumen, and place on top of the oven until practically all of the carbon disulfide has been driven off. Place in the oven at  $110^{\circ} \pm 10^{\circ}\text{C.}$  for at least 20 minutes. Cool in a desiccator and weigh.

(c) If insoluble matter adheres to the beaker, dry the beaker in the oven at

110°C. and weigh. Add the weight of this adherent material as a correction to the weight of the insoluble matter in the Gooch crucible.

(d) Ignite the evaporating dish to a dull red heat, cool in a desiccator and weigh. Pour the filtrate from the filtering flask into the dish and wash the flask thoroughly with carbon disulfide, putting these washings into the dish also. Burn off the carbon disulfide in a hood and ignite the residue until no black or glowing spots remain. Extreme care must be exercised during the ignition to prevent the light mineral matter from being blown out of the dish. Cool in a dessicator and weigh immediately. This weight shall be added as a correction to the weight of the insoluble matter in the Gooch crucible.

(e) If a determination of mineral matter be required, ignite the Gooch crucible from paragraph (b) at a red heat until any black or glowing spots are burned off. Cool in a desiccator and weigh. The corrections described in paragraphs (c) and (d) shall be added to the weight of mineral matter in the Gooch crucible. If a carbonate mineral is present, add to the ignited mineral matter a few drops of ammonium carbonate solution, dry at 100°C., heat for a few minutes to a dull red heat, cool in a desiccator and weigh.

(f) The weight of filter aid used must be subtracted from the total weight of insoluble residue and also from the total weight of mineral matter in the Gooch crucible in order to obtain net weights.

Calculations and Report.—Calculate the bitumen content, mineral matter, and difference as follows:

$$\text{Bitumen content, \%}, X = \frac{A - (B + D)}{A} \times 100$$

$$\text{Mineral matter, \%}, Y = \frac{C + D}{A} \times 100$$

$$\text{Difference} = 100 - (X + Y)$$

where  $A$  = weight of water-free sample

$B$  = net weight of insoluble residue

$C$  = net weight of ignited mineral matter

$D$  = total weight of correction

Report the bitumen content as a percentage by weight of the water-free material. Also report mineral matter and difference, if required, as percentages by weight of the water-free material. Report whether Procedure No. 1 or No. 2 was used.

## CARBENES

The expression "carbenes" has been applied to that portion of bituminous substances soluble in carbon disulfide but insoluble in carbon tetrachloride. This test is of value in identifying bituminous substances, gauging their uniformity of supply, for purposes of factory control, and as a criterion of their quality. Certain hard native asphalts and asphaltites, particularly grahamite, normally contain a percentage of carbenes, whereas petroleum asphalts do not show carbenes unless they are overheated or overblown. If more than 0.5% is present in petroleum asphalts, their quality is to be regarded as questionable. Carbenes are found in tars and pitches in varying amounts.

Although carbenes are found in grahamite and certain hard natural asphalts when tested as such, they disappear upon fluxing to a softer consistency. With petroleum asphalts, tars, and pitches, the carbenes are of a different character, since they are insoluble in fluxes and do not disappear upon being so treated.

The procedure for the determination of bitumen soluble in carbon tetrachloride has been standardized as follows as ASTM D165-42:

**Procedure.**—An amount of material which shall contain approximately 1 g. of bitumen shall be weighed into a tared Erlenmeyer flask. One hundred milliliters of chemically pure carbon tetrachloride shall be added to the flask in small portions with continued agitation until all lumps disappear and nothing adheres to the bottom. The flask shall be corked and set aside in subdued light for at least 12 hours.

The Gooch crucible, prepared as for the determination of bitumen soluble in carbon disulfide shall be set up with the suction flask and the carbon tetrachloride solution carefully decanted through the asbestos felt, with or without light suction as may be found necessary. No sediment shall be allowed to go onto the filter. A small amount of carbon tetrachloride shall be used to wash down the sides of the flask and then the precipitate shall be brought onto the felt and the flask scrubbed with a feather if necessary to remove all precipitate. The contents of the crucible shall be washed with carbon tetrachloride until the washings are colorless. Suction shall be applied to the crucible to remove the carbon tetrachloride. The crucible shall be dried in the oven at 100° to 125°C. for 20 minutes, cooled in the desiccator, and weighed.

In case insoluble matter adheres to the flask, it shall be dried and weighed, and the increase in weight over the original weight shall be added to the weight of insoluble matter in the crucible.

In case there is any question involving the amount of mineral matter that may have passed through the filter, evaporate the filtrate and burn the bituminous residue. If a carbonate mineral is present in the filtrate ash, add to the ash a few drops of ammonium carbonate solution, and dry at 100°C., then heat for a few minutes to a dull red heat, and cool in the desiccator. Weigh and add the weight of the ash obtained to the weight of matter insoluble in carbon tetrachloride.

The proportion of bitumen soluble in carbon tetrachloride shall be reported on the basis of total bitumen taken as 100:

Proportion of bitumen soluble in carbon tetrachloride

$$= \frac{\text{bitumen soluble in carbon tetrachloride}}{\text{total bitumen}}$$

The difference between the percentages soluble in carbon disulfide and carbon tetrachloride, respectively, represents the per cent of "carbenes."

### SOLUBLE IN PETROLEUM NAPHTHA

This test is employed mainly for purposes of identification. It is also used to a certain extent for determining the adaptability of bituminous substance for a given use, for gauging the uniformity of supply, and for purposes of factory control. As a general principle, the harder the bituminous product, the smaller will be the percentage that dissolves in petroleum naphtha. Asphaltites are relatively insoluble in this menstruum. Mineral waxes, peat-, lignite- and shale-tars or pitches are largely soluble. The solubility of native and petroleum asphalts varies, depending largely



upon their hardness, and also in the case of petroleum asphalts upon the extent to which the distillation has been carried. Coal-tar pitches are relatively insoluble in 88° Baumé petroleum naphtha.

The portion soluble in petroleum naphtha has been termed "petrolenes" by some, and "malthenes" by others, whereas the nonmineral constituents insoluble in naphtha are generally referred to as "asphaltenes."

It is important that the petroleum naphtha should be derived from petroleum composed entirely of open-chain hydrocarbons, and test exactly 88° Baumé, equivalent to a specific gravity of 0.638 at 60°F./60°F. At least 85% by volume should distill between 95° and 150°F. The density and character of the naphtha is important, since heavy distillates, or products derived from petroleum containing unsaturated or cyclic hydrocarbons, will exert a greater solvent action upon the bituminous substance.

The results will be more consistent if the petroleum spirits is first washed with fuming sulfuric acid to remove the aromatic constituents. There appears to be no difference in the results if the precipitation is carried out at any temperature between 0° and 32°C. As the boiling point of the petroleum spirits employed in making the test increases, the quantity of precipitate decreases. The fraction below 105°F. appears to give the most reliable results.

Asphaltenes show increasing solubility in solvents in the order of their surface tension (e.g., ether, benzol, carbon disulfide, and pyridine). Ether has been recommended as a substitute for petroleum naphtha because it is a homogeneous substance, not requiring standardization, and in addition has good flocculating properties and exerts a greater solvent action on hydroxy acids present in certain asphalts.

This method is performed in the same manner as for determining the portion soluble in carbon disulfide, petroleum naphtha being substituted for the latter. Hard bituminous substances should be powdered; liquid bituminous substances flowed in a thin layer over the bottom of the flask; and semisolid to semiliquid substances heated until fluid and distributed in a thin layer to present a greater surface to the solvent. It is advisable not to use a stirring rod, as this causes the bituminous substance to adhere to the inner surface of the flask and to the rod itself. The operation should take place at room temperature, and away from the direct rays of the sun. The introduction of a weighed portion of long-fibered asbestos to the solution will assist in its filtration.

This method has been standardized by the American Association of State Highway Officials under the designation of AASHO T46-35. It is not an ASTM Standard Method.

The percentage of asphaltenes varies considerably; thus, with asphalts all having the same R. and B. fusing point of 140°F., the following are obtained: extracted asphalt from Trinidad asphalt 37%, Mexican residual asphalt 20%, California residual asphalt 12%, Colombian residual asphalt 16%, Illinois residual asphalt 12%, Texas residual asphalt 9 to 17%.

#### BENZENE INSOLUBLE ("FREE CARBON")

This test is generally used for testing tars and pitches for the presence of non-mineral matter insoluble in hot benzene. The test is of value for purposes of identification, for ascertaining the adaptability of the tar or pitch for a given purpose, and for gauging its uniformity of supply. Tars and pitches containing large percentages of insoluble matter, known as "free carbon," are objectionable for certain

manufacturing purposes, since the free carbon acts as so much inert matter. The term "free carbon" is a misnomer, since it is not elemental carbon, but a complex mixture of hydrocarbons of high molecular weight, containing 90.0 to 91.7% carbon, 3.4 to 4.0% hydrogen, 1.0 to 1.2% nitrogen, 2.5 to 3.3% oxygen and 0.7 to 1.4% sulfur, on the ash-free basis. The presence of hydrogen has been explained by the great absorptive power of carbon in its pure state, which retains hydrocarbons tenaciously, as well as hydrogen, which is not driven off at temperatures as high as 800°C. Free carbon is more soluble in aniline or pyridine than in benzene or carbon disulfide. Selenium oxychloride exerts the greatest solvent action upon it, but unfortunately the residue cannot be freed from this solvent. It is also partially decomposed by digesting with hot fuming nitric acid.

The determination of benzene-insoluble matter has been standardized by the ASTM under the designation D367-49 and is performed as follows:

These methods are intended for the determination of benzene-insoluble matter in creosote and creosote-coal tar solutions. The asbestos mat method is the preferred method, whereas the porous thimble method may be used as an alternate. The asbestos mat method gives accurate results and requires 3 or 4 hours less time than the porous thimble extraction method.

### ASBESTOS MAT METHOD

**Apparatus and Materials.**—The apparatus and materials shall consist of the following:

- (a) Filter Flask with crucible holder and means for producing a vacuum.
- (b) Asbestos Fiber.—A water suspension of medium-fiber acid-washed asbestos containing from 10 to 15 g. of asbestos per liter.
- (c) Filtering medium consisting of a Coors No. 3, or equivalent, Gooch filtering crucible approximately 35 mm. in diameter at the top, 22 mm. at the bottom, and 40 mm. in height, containing a mat of medium-fiber acid-washed asbestos weighing at least 0.5 g.
- (d) Balance sensitive to 0.5 mg.
- (e) Benzene, 2° distillation range, conforming to the Standard Specifications for Industrial Grade Benzene (ASTM D836-50).
- (f) Acetone, c.p.

**Preparation of Filter Mat.**—Place the weighed Gooch crucible in the holder on the filter flask and pour in about 5 ml. of the well-shaken asbestos suspension. Let stand for about 1 minute; then apply gentle suction and suck the mat dry. Add in four increments the amount of suspension calculated to produce a mat weighing 0.5 g. When the required amount of asbestos has been added, wash the sides of the crucible free of particles and wash the mat at least three times with distilled water to ensure the removal of any loose material. Suck the crucible dry, remove it from the holder, and dry for at least 1 hour at  $105^{\circ} \pm 5^{\circ}\text{C}$ . Cool in a desiccator and weigh.

**Procedure.**—Use the original undehydrated sample. If necessary, heat the sample and stir until any crystalline material is in solution and the sample is homogeneous.

Weigh the following size of sample, to the nearest 0.01 g., into a 100-ml. beaker or 125-ml. Erlenmeyer flask:

New grade I creosote, g.....	10 $\pm$ 1.0
Used creosote and grade A solution, g.....	5 $\pm$ 0.5
Grades C and B solutions, g.....	2.0 $\pm$ 0.1

Warm 50 ml. of benzene to a temperature of 50° to 60°C. and immediately add it to the sample, while stirring thoroughly. Continue stirring until the sample is dispersed and the bottom of the beaker is clean. Bring the beaker or flask containing the solution to boiling on a hot plate.

Weigh a prepared crucible and mount in the section apparatus. Fill the crucible halfway with boiling benzene and, with the suction turned on, slowly pour the mixture containing the sample into the crucible before the solution first introduced has been drawn entirely through the asbestos mat. Take care that the mat is never free from liquid, either during the addition of the solution containing the sample or during the subsequent washing with benzene. *This is very important.* Wash the beaker or flask with hot benzene, using a policeman until clean, and adding the washings to the crucible. Wash the crucible and contents with hot benzene until the washings are colorless. Reduce the suction and wash the contents with acetone until the washings are colorless. Four additions of approximately 5 ml. each are usually sufficient.

Remove the crucible from the holder and wipe the outside clean with a paper wet with benzene. Dry at 105° ± 5°C. for 20 minutes, cool in a desiccator, and weigh.

Determine the percentage of water in the original sample in accordance with the Standard Method of Test for Water in Creosote (ASTM D370-58).

Calculation.—Calculate the benzene-insoluble matter as a percentage of the water-free preservative, as follows:

$$\text{Benzene-insoluble matter, \%} = \frac{100(A - B)}{C} \times \frac{100}{(100 - D)}$$

where  $A$  = weight of crucible after filtration, in grams

$B$  = weight of prepared crucible before filtration, in grams

$C$  = weight of sample used, in grams

$D$  = percentage of water in the sample

### POROUS THIMBLE METHOD

**Apparatus and Materials.**—The apparatus and materials shall consist of the following:

(a) Extractor of the form shown in Fig. 28-16, in which a thimble containing the sample is subjected to direct washing by the hot solvent. The extraction flask is fitted with a metal cap condenser.

(b) Filtering medium consisting of a flat-bottom, 30- by 80-mm., RA 98 alundum thimble. It shall be suspended within the extraction flask in a wire basket hung from the condenser.

(c) Balance sensitive to 0.5 mg.

(d) Benzene, 2° distillation range, conforming to ASTM Specifications D836-50.

**Procedure.**—Use the original undehydrated sample. If necessary, heat the sample and stir until any crystalline material is in solution and the sample is homogeneous.

Weigh the following size of sample, to the nearest 0.01 g., into a 100-ml. beaker or 125-ml. Erlenmeyer flask:

New grade I creosote, g.....	10 ± 1.0
Used creosote and grade A solution, g.....	5 ± 0.5
Grades B and C solutions, g.....	2.0 ± 0.1

Warm 50 ml. of benzene to a temperature of 50° to 60°C. and immediately add it to the sample, while stirring thoroughly. Continue stirring until the sample is dispersed and the bottom of the beaker is clean.

Prepare the thimbles for use by removing any insoluble material with a brush and igniting at a bright red heat in a muffle or over a Meker burner until any combustible material has been burned off. Cool somewhat; then cool to room temperature in a desiccator and weigh.

Wet a thoroughly clean, ignited and weighed thimble with approximately 10 ml. of benzene, pour out the excess, and immediately transfer the benzene solution of

the sample into the wetted thimble; the solution shall not more than half fill the thimble at any time. Wash the beaker or flask with benzene, rub with a rubber policeman, and add the washings to the thimble.

As soon as all the washings have been added to the thimble, place in the extraction apparatus, which shall contain approximately 100 ml. of benzene. Heat sufficiently to maintain a continuous dropping of benzene from the condenser coil at a rate of not less than 60 drops per minute and a maximum rate that will leave 15 mm. of the thimble empty. Continue the extraction until solvent dropping from the thimble is colorless, but for a period of at least 3 hours.

After extraction, remove the thimble from the flask and allow to drain free from benzene. Dry the thimble

at 105° ± 5°C. for not less than 60 minutes, cool in a desiccator, and weigh.

**Calculation.**—Calculate the benzene-insoluble matter as a percentage of the water-free preservative, as follows:

$$\text{Benzene-insoluble matter, \%} = \frac{100(A - B)}{C} \times \frac{100}{(100 - D)}$$

where  $A$  = weight of thimble after extraction, in grams

$B$  = weight of clean thimble before extraction, in grams

$C$  = weight of sample used, in grams

$D$  = percentage of water in the sample

The ASTM method above has special reference to creosote and creosote-coal-tar solution. It may be used for coal-tar pitches, in which case the porous thimble alternate method should be used.

Various modifications of the above method are in common industrial use.

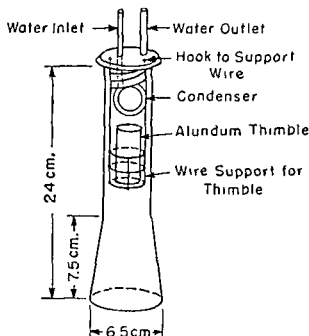


FIG. 28-16. Extraction Flask. (Courtesy ASTM)

## TOLUENE INSOLUBLE

This test is usually performed by heating the pitch sample in toluene at 90° to 100°C. and filtering through a sintered crucible. The test has been standardized by the Standardization of Tar Products Tests Committee (British) as Serial No. P.T. 7-57.

A typical modified method is performed as follows:

Pour 60 ml. of toluene into a 100-ml. beaker containing the crushed and weighed sample, stirring continuously to ensure complete mixture of the sample and toluene and thorough dispersing of the insoluble matter. Place the beaker immediately on a steam bath or water bath, heat the solution to from 90° to 100°C. and maintain at this temperature for a period of not less than 20 nor more than 30 minutes. Stir occasionally during this period and make certain that the sample is completely dispersed in the toluene.

Filter the hot toluene solution through a previously prepared and weighed extraction thimble and use small additional quantities of toluene to transfer the insoluble material to the thimble. When substantially all the toluene has drained from the thimble, wash the thimble and its contents once with a small quantity of benzene.

Place the drained thimble in the extraction apparatus and extract with refluxing benzene as in ASTM D367-49 except that the time of extraction shall be not less than 18 hours and not more than 24 hours.

## QUINOLINE INSOLUBLE

This test has not been standardized, but a typical method of performing the test follows.

*Apparatus.*—The apparatus shall consist of:

- (a) Suction flask, 500-ml. capacity.
- (b) Filtering crucibles, Selas porcelain, medium porosity.
- (c) Crucible holders.
- (d) Water bath, maintained at 70° to 80°C.
- (e) Drying oven, maintained at 105° to 110°C.
- (f) Filter aid, Celite 505 (NOTE).

NOTE.—Celite gains weight slowly when exposed to air; therefore rapid weighing is essential for accuracy.

*Reagents.*—The special reagents required are:

- (a) 95% quinoline, F.P. -19.0°C. minimum 95% shall distill within 2°C. including the temperature of 237.1°C.
- (b) Benzene, pure grade.

*Procedure.*—Prepare a filtering crucible with a layer of approximately 0.5 g. of filter aid, and dry in an oven for 30 to 60 minutes at 105° to 110°C. Cool in a desiccator and weigh quickly for the tare weight (NOTE).

NOTE.—Crucibles must be cleaned before each test by removing the mat, washing, drying, and igniting in a muffle furnace at approximately 950°C. for sufficient time to clean the crucible. After six tests the crucible should be washed in hot dilute hydrochloric acid to clear residual ash from the filter pores.

Accurately weigh from 1 to 5 g. of sample (NOTE) and place in a 100-ml. beaker containing another 0.5000 g. of dried filter aid. Add 25 ml. of quinoline and digest on a water bath at 70° to 80°C. for 15 minutes, stirring occasionally. Filter

through the prepared crucible, first wetting the crucible with a little quinoline and starting the suction before filtering. Rinse the beaker with another 25-ml. portion of warm quinoline. Police and wash the beaker and filter with small portions of benzene using a total of 100 ml. of benzene. Allow filter to drain completely between each washing.

NOTE.—Sample weight should be such as to yield 0.1 g. of quinoline insoluble.

Suck the crucible dry for several minutes, then place in an oven for 30 minutes at 105° to 110°C. Cool in a desiccator and weigh quickly.

$$QI \% = \frac{A - B - C}{D}$$

where  $QI$  = quinoline insoluble

$A$  = final gross weight of the crucible (wt. of quinoline insol. + filter aid added to sample + tare wt. of crucible)

$B$  = weight of filter aid added to sample (0.5000 g.)

$C$  = tare weight of prepared crucible

$D$  = weight of sample taken

### ANTHRACENE OIL INSOLUBLE

A typical method of performing this test requires an anthracene oil as follows:

Specific gravity at 15°C.....	1.085
Distillate to 250°C., maximum.....	10%
Distillate to 315°C., minimum.....	32%
Distillate to 355°C., maximum.....	51%
Distillate to 355°C., minimum.....	64%

A 2-g. sample of the pitch is placed in a flask and 100 ml. of anthracene oil added. Any water in the oil is driven off, and the material heated under reflux for 30 minutes. The hot solution is then filtered through a weighed Pyrex filtering crucible and the insoluble material washed with hot pyridine and benzene.

## CHEMICAL TESTS

### DETERMINATION OF WATER

The estimation of water is made in some cases for purposes of identification, and in others as a criterion of the quality. Native asphalts and tars are examined in this way to ascertain whether they exist in the crude or the dehydrated state. This test is also used for dehydrating bituminous substances to render them suitable for further examination, where the presence of water would interfere.

This method is adapted to crude petroleum, tars, creosote oil, and other fluid bituminous substances and is standardized as ASTM D370-58.

**Apparatus.**—The apparatus is set up as shown in Fig. 28-17. The copper still is provided with a removable flanged top and yoke of the form and approximate dimensions shown in Fig. 28-18.

The condenser consists of a copper trough carrying a straight-walled glass tube. The separatory funnel has a total capacity of 120 ml. with the outlet graduated in fifths of a milliliter.

**Procedure.**—Pour 200 to 500 ml. of bituminous material into the still and weigh. Clamp the top in place, using a paper gasket moistened with lubricating oil. Apply

heat with the ring burner supported just above the level of the bituminous material at the beginning of the test, and then gradually lower it as the water distills over. Continue the distillation until the vapor temperature reaches 205°C. Collect the

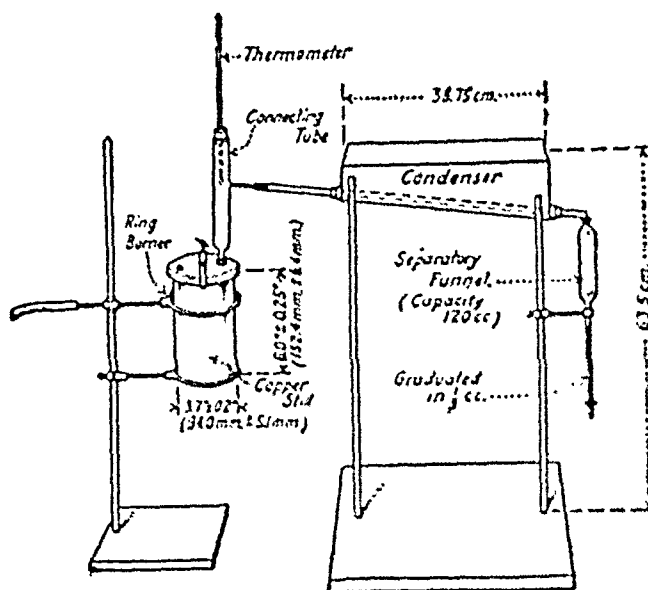


FIG. 28-17. Assembled Apparatus for Water Test. (Courtesy ASTM.)

distillate in the separatory funnel, and let it stand until a clean separation of water takes place. Read off the volume of water, calculate its weight, and figure the per cent present in the crude bituminous material.

When it is desired to determine the percentage of moisture without using the residue for other purposes, a convenient method consists in distilling it with a solvent. The following procedure has been standardized as ASTM D95-58.

**Apparatus.**—The apparatus shall consist of a metal still or glass flask, heated by suitable means and provided with a reflux condenser discharging into a trap connected to the still or flask. The trap serves to collect and measure the condenser water and to return the solvent to the still. The type of distilling apparatus used is not an essential feature of this method, but glass has been generally used for petroleum products and the metal still for road materials and tars.

(a) The metal still (Fig. 28-19 (a)) shall be a vertical cylindrical vessel, preferably of copper, having a faced flange at the top to which the head is tightly attached by means of a clamp. The head shall be of metal, preferably of brass or copper, and be provided with a tubulation 1 in. in inside diameter.

(b) The glass flask (Fig. 28-19 (b)) shall be of the short-neck, round-bottom type, made of well-annealed glass, having an approximate capacity of 500 ml.

(c) The burner used with the metal still shall be a ring gas burner 4 in. (100 mm.)

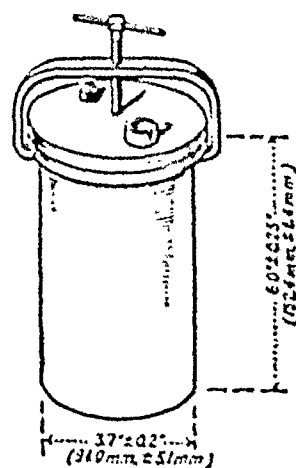


FIG. 28-18. Copper Still. (Courtesy ASTM.)

in inside diameter. With the glass flask, an ordinary gas burner or electric heater may be used as the source of heat. The condenser shall be of the water-cooled, reflux, glass-tube type, having a condenser jacket not less than 400 mm. (15¾ in.) in length with an inner tube 9.5 to 12.7 mm. (¾ to ½ in.) in outside diameter. The end of the condenser to be inserted in the trap shall be ground off at an angle of 30° from the vertical axis of the condenser.

(d) The trap shall be made of well-annealed glass constructed in accordance with Fig. 28-19 (c) and shall be graduated as shown, from 0 to 10 ml. in 0.1-ml. divisions.

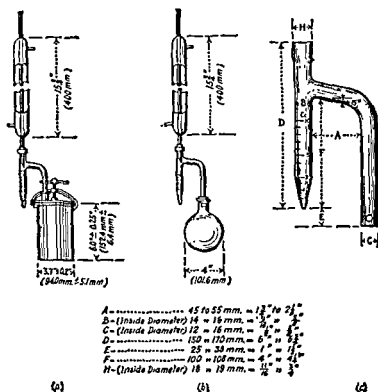


FIG. 28-19. Apparatus for Water Test. (Courtesy ASTM.)

The error of any indicated capacity shall not be greater than 0.05 ml. The outside diameters should be preferably 2.5 to 3.5 mm. (3/32 to 1/8 in.) greater than the inside diameters specified.

**Solvent.**—(a) The solvent used when testing petroleum products or bituminous materials derived from petroleum shall be a petroleum distillate, free from water, and shall conform to the following distillation requirements:

5% shall distill at a temperature not below 194°F. (90°C.) nor above 212°F. (100°C.)  
 90% shall distill below 410°F. (210°C.)

(b) The solvent used when testing bituminous materials derived from coal tar, water-gas tar, etc., shall be xylene or a blend of 20% benzene and 80% xylene.

**Sample.**—The sample shall be thoroughly representative of the material to be tested and the portion of the sample used for the test shall be thoroughly representative of the sample itself. Deviation from this requirement shall not be permitted.



**NOTE.**—The difficulties in obtaining proper representative samples for this determination are unusually great so that the importance of sampling cannot be too strongly emphasized.

**Procedure.**—When the sample to be tested contains less than 10% of water, exactly 100 ml. of the material to be tested shall be placed into the still or flask and thoroughly mixed with an equal volume of solvent by swirling, proper care being taken to avoid any loss of material. If the material is measured by volume, an accurate 100-ml. graduated cylinder shall be used and the contents transferred to the still by rinsing with one 50-ml. portion of solvent, followed by two successive 25-ml. portions of solvent, the cylinder being allowed to drain each time. When the sample to be tested contains more than 10% of water, the volume of material used shall be decreased to that which will yield somewhat less than 10 ml. of water.

**NOTE.**—In special cases where the water content exceeds 10% and it is not desirable to reduce the size of the sample to that which will yield somewhat less than 10 ml. of water, a distilling tube receiver graduated from 0 to 25 ml. may be used. This tube shall be graduated from 0 to 2 ml. in 0.1 ml., from 2 to 5 ml. in 0.2 ml. and from 5 to 25 ml. in 0.5 ml.

The connections between the still or flask, trap, and condenser shall be made by means of tight-fitting corks or standard taper ground joints. When the metal still is used, a heavy paper gasket moistened with the solvent shall be inserted between the lid and flange before attaching the clamp. A loose cotton plug shall be inserted in the top of the condenser tube to prevent condensation of atmospheric moisture in the condenser tube. The condenser tube and trap must be chemically clean to assure free drainage of water into the bottom of the trap.

Heat shall then be applied and so regulated that the condensed distillate falls from the end of the condenser at the rate of from two to five drops per second. The ring burner used with the metal still should be placed about 3 in. above the bottom of the still at the beginning of the distillation and gradually lowered as the distillation proceeds.

The distillation shall be continued at the specified rate until no water is visible on any part of the apparatus except at the bottom of the trap. This operation usually requires less than an hour. A persistent ring of condensed water in the condenser tube shall be removed by increasing the rate of distillation or cutting off the condenser water for a few minutes.

The volume of condensed water measured in the trap at room temperature multiplied by 100 and divided by the volume of the sample used shall be the percentage of water and shall be reported as “. . . % water by volume, ASTM method.”

The accuracy to be expected with this method is that duplicate determinations of water should not differ from each other by more than one division on the trap.

### SULFONATION RESIDUE

The sulfonation residue test is useful for distinguishing between materials of petroleum origin which have a high residue and materials of coal-tar origin which have a low residue.

The test is performed by heating the sample with 37 *N* sulfuric acid and measuring the volume of the unsulfonated oil.

The test has been standardized by the ASTM under the designation D872-48 and is performed as follows:

This method covers the test for determination of the sulfonation index of road tars. The method is intended for use in determining the sulfonation index of the total distillate to 300°C. (572°F.), or of the fraction of the distillate from 300° to 355°C. (572° to 671°F.), obtained by distillation of the road tar in accordance with the Standard Method of Test for Distillation of Tar Products Suitable for Road Treatment (ASTM D20-56).

The sulfonation index of road tar is the number of milliliters of unsulfonated residue per 100 g. of tar when determined in accordance with this method.

**Apparatus.**—The apparatus shall consist of the following:

(a) **Test Bottles.**—The test bottles shall be made of good quality glass and shall be 6-in., 18-g., either 8 or 10%, Babcock milk test bottles. The capacity to the base of the neck shall be 45 to 50 ml. The graduated portion of the bottle shall contain  $1.60 \pm 0.025$  ml. for the 8% test bottle and  $2.00 \pm 0.025$  ml. for the 10% test bottle (at a temperature of 25°C. (77°F.)) The 8% test bottle shall be graduated in eight major divisions with each major division further divided into ten subdivisions, and the 10% test bottle shall be graduated in ten major divisions with each major division further divided into five or ten subdivisions. Each line for the major divisions shall extend at least three-fourths of the way around the neck and be numbered from the bottom 1, 2, etc. Within the range from 0 to 8 for the 8% test bottle and 0 to 10 for the 10% test bottle, the maximum error in volume shall not be greater than 0.025 ml. The graduation marks shall be clear and fine, not more than 0.3 mm. in width. The body of the bottles shall have a ground area of at least 2 sq. cm. for numbering.

(b) **Water Baths.**—Two water baths, as follows:

1. A water bath maintained at  $25^\circ \pm 0.3^\circ\text{C}$ . ( $77^\circ \pm 0.5^\circ\text{F}$ .) and of such depth that, when a test bottle is immersed, the upper level of its contents is below the surface of the water.

2. A water bath maintained at  $98^\circ$  to  $100^\circ\text{C}$ . ( $208^\circ$  to  $212^\circ\text{F}$ .) and of sufficient depth to permit complete immersion of the body of the test bottle.

**Reagents.** (a) **Sulfuric Acid, 37 N.**—Prepare 37 N  $\text{H}_2\text{SO}_4$  by blending reagent-grade fuming and concentrated sulfuric acids to  $98.61 \pm 0.2\%$   $\text{H}_2\text{SO}_4$ , as determined by titration.

(b) **Sulfuric Acid, sp. gr. 1.84.**

**Procedure.**—(a) Weigh  $5 \pm 0.1$  g. of the distillate or fraction of distillate (first paragraph) into the test bottle. If the distillate contains solid matter, warm the distillate in a hot-water bath, while stirring until the solid matter has melted before taking the sample for testing.

(b) Slowly add 10 ml. of 37 N  $\text{H}_2\text{SO}_4$  to the test bottle from the buret in such a way as to wash down any distillate remaining in the neck of the bottle. Shake the test bottle for 2 minutes. Do not allow the temperature of this acid-distillate mixture to approach  $100^\circ\text{C}$ . ( $212^\circ\text{F}$ .), as indicated by the bottle becoming too warm to touch, or by the contents foaming excessively; cool the test bottle in ice water if necessary. If the distillate contains solid matter that does not readily disperse in the acid, warm the acid-distillate mixture in the hot-water bath to liquefy the solid matter.

(c) Add 10 ml. more of 37 N  $\text{H}_2\text{SO}_4$  as described in paragraph (b), and shake the

bottle vigorously for 30 seconds. Then place the test bottle in the water bath maintained at 98° to 100°C. (208° to 212°F.).

(d) After the test bottle has been in the bath for 10 minutes remove it, shake vigorously for 30 seconds, and replace immediately in the water bath maintained at 98° to 100°C. (208° to 212°F.). If the acid-distillate mixture boils over at this stage, discard it and repeat the test.

(e) Repeat the procedure described in paragraph (d) for a total of six 10-minute immersions and shakings. After the last shaking, allow the bottle to cool approximately to room temperature.

(f) Add sufficient  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) to the contents of the test bottle to raise the liquid level in the neck to near the top of the graduations. Place the test bottle and its contents in the centrifuge and whirl at a speed of approximately 1000 r.p.m. for 5 minutes. Remove the bottle from the centrifuge and place in the water bath at 25°C. (77°F.) so that the contents of the bottle are immersed below the surface of the water. After 10 minutes remove the test bottle from the bath and read the volume of the oil to within one-tenth of a major division. Repeat the centrifuging until the volume of oil is constant.

(g) Generally, the unsulfonated residue is a clear transparent oil. Occasionally some white or even dark-colored solids may be present. In case solid materials appear that cannot be melted in the water bath without causing overflow of the bottle, make a new test. Follow the same procedure as described in paragraphs (a) to (f), except that upon removing the bottle from the hot-water bath, after the six immersions and shakings [paragraph (e)], fill it immediately with  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) to a point below the top of the graduations to allow room for expansion. Whirl the bottle in the centrifuge for 3 minutes and again heat for 5 minutes in the water bath maintained at 98° to 100°C. (208° to 212°F.). Repeat this cycle until the volume of the oil is constant. Make the final reading of the volume while the test bottle is immersed in the hot-water bath at 98° to 100°C. (208° to 212°F.). Any material that is solid at this temperature (resins) shall not be included as unsulfonated residue.

(h) After a constant oil volume has been obtained by centrifuging, note the difference in the readings of the upper and lower menisci of the separated oil. Multiply by 0.2 to obtain the number of milliliters of unsulfonated residue in the sample.

**Precautions.**—(a) It is extremely important that all glassware used in this test shall have been thoroughly cleaned and dried before use.

(b) The required amount of vigorous shaking is very important, and in no case shall the designated number of shakings or the time of shaking be decreased below the limits set. It is also important that the shaking shall be such that the distillate will be completely dispersed through the acid at the conclusion of each shaking period. If excess foaming results from the shaking after any heating interval, the bottle shall be cooled for 15 or 20 seconds in a cold-water bath, after which the shaking can usually be continued without foaming of the contents.

(c) The rate of whirling may be decreased to avoid breakage of the test bottles. In all cases, however, the centrifuging shall be continued until a constant reading of the volume of unsulfonated residue is obtained.

(d) If a separate layer of unsulfonated residue cannot be readily observed because of its being dark colored or because of the presence of solids, a few drops of a solution of NaOH (100 g. per l.) shall be added, by means of a pipet, to the

## 1000 EXAMINATION OF BITUMINOUS SUBSTANCES

bottle. Any portion soluble in this reagent shall not be included as unsulfonated residue.

**Calculation and Report.**—(a) Calculate the sulfonation index as follows:

$$\text{Sulfonation index} = \frac{AB}{C}$$

where *A* = milliliters of unsulfonated residue in the sample [paragraph (h) under Procedure]

*B* = percentage, by weight, of distillate in the tar

*C* = weight in grams of the sample of distillate

(b) Report the sulfonation index to the nearest 0.1

### SAPONIFIABLE CONSTITUENTS

Certain bituminous substances, such as montan wax, rosin pitch, and fatty-acid pitch, are often composed largely of saponifiable constituents. Others, including pine tar, pine-tar pitch, hardwood tar, hardwood-tar pitch, peat tar, lignite tar, bone tar, bone-tar pitch, and other forms of fatty-acid pitches, contain smaller percentages. This test is also used for gauging the uniformity of supply, and in the case of fatty-acid pitches, as a criterion of the quality.

**Procedure.**—The following procedure may be used for examining bituminous materials or admixtures of bituminous materials with animal or vegetable oils and fats, since the customary methods do not adapt themselves especially well, due to the formation of troublesome emulsions. The bituminous material is first freed from insoluble constituents, including any mineral matter, by boiling with benzene under a reflux condenser, cooling, and filtering through a Gooch crucible. The insoluble constituents are dried at 100°C. and weighed. Sufficient of the bituminous substance should be taken to yield approximately 5.0 g. of extract. The benzene solution is evaporated or distilled to 50 ml. and 50 ml. of the saponifying liquid added from a pipet. This should consist of a 10% solution of caustic potash, prepared by dissolving 100 g. of anhydrous potash in 500 ml. of 95% ethyl alcohol, and diluting to a liter with 90% benzene. The liquid is allowed to stand overnight to permit any carbonate to settle, and the clear solution is decanted. After the saponifying agent is added, the mixture is boiled under a reflux condenser, for 30 to 60 minutes, and the contents of the flask, while still warm, poured in a separatory funnel containing 150 ml. of boiling water and 25 ml. of a 10% solution of potassium chloride. Add 250 ml. of benzene, agitate vigorously, and allow the funnel to rest quietly in a warm place until the solvent separates. If an emulsion forms which refuses to separate on standing, add 200 ml. more benzene and 100 ml. 95% ethyl alcohol and stand in a warm place overnight. This will invariably effect a more or less complete separation of the solvent. From this point on the method is illustrated by the tabular outline on p. 1001.

In the case of bituminous materials that are more or less completely saponifiable, the intermediate layer is apt to be absent. In this case the process will simplify itself considerably. The foregoing procedure will separate the unsaponifiable constituents in practically an ash-free state.

Saponify as described.

Draw off the soap solution as completely as possible.

Decant the benzene layer, leaving the intermediate layer in the separatory funnel.

Aqueous Soap Solution. Exhaust with 200-ml. portions of benzene.		Benzene Layer.	Intermediate Layer.
Aqueous Soap Solution.	Combined Benzene Extracts.		
	Combine and exhaust with 100-ml. por- tions of 50% alcohol.		
	Benzene Solution.	Combined Alcoholic Extracts.	
		Combine and exhaust with benzene.	
		Combined Benzene Extracts.	Alcoholic Soap Solu- tion.
Combined evaporate to a small bulk, com- plete the evaporation at 100°C., cool and weigh the <i>Unsapoifiable Constituents</i> .			
Combine			

Acidify with dilute hydrochloric acid, warm, and exhaust with benzene. Separate the aqueous solution containing the glycerol and mineral salts. Evaporate the combined benzene extracts to a small bulk, and then complete the evaporation of solvent at 100°C. Cool and weigh. Weight equals the *free acids derived from the saponifiable constituents*.

## DIAZO REACTION

This test is used for identifying bituminous substances containing phenols, including wood tar and wood-tar pitch, oil-gas- and water-gas-tars and pitches, shale tar, peat- and lignite-tars and pitches, bone-tar, bone-tar pitch and the various coal-tar pitches.

This reaction is carried out by boiling 2 g. of the bituminous substance with 20 ml. *N* aqueous sodium hydroxide, for approximately 5 minutes. After cooling, the liquid is filtered. If the filtrate is dark colored, it may be lightened by shaking with finely pulverized sodium chloride and filtering. It is then cooled in ice to 10°C., and a few drops of freshly prepared benzenediazonium chloride solution added (prepared by dissolving 1 g. aniline hydrochloride in 10 ml. water and 3 ml. 25% hydrochloric acid, and then adding drop by drop, a saturated solution of 0.5 g. sodium nitrite in water). To avoid the preparation of benzenediazonium chloride (which does not keep), the use of *p*-diazobenzenesulfonic acid may be substituted, since it is a more stable chemical and will keep well in stock. If phenols are pres-

ent, a more or less fugitive red coloration will result, sometimes accompanied by a reddish precipitate.

Assuming that the bituminous substance gives the diazo reaction, the question will often arise whether the product is a straight-distilled pitch, or an asphalt "cut-back" with a high boiling-point distillate containing phenolic bodies, derived from coal tar, lignite tar, etc. Marcusson has worked out a method applicable under these circumstances, which consists in dissolving 10 g. of the bituminous substance in 15 ml. of benzene, and pouring the solution into 200 ml. of 88° petroleum naphtha. The resulting precipitate is filtered and washed with petroleum naphtha and dried. It is then boiled for 15 minutes with 0.5 *N* alcoholic caustic potash under a reflux condenser to extract the phenols. The liquid is cooled and filtered, the alcohol evaporated, and the residue dissolved in water. Sodium chloride is added to clarify the liquid and remove any substances imparting a dark color, the solution is filtered and the filtrate treated for the diazo test described above. If a straight-distilled pitch containing phenols is present, a positive reaction will be obtained. If the original substance gives the diazo test, but the residue treated in the above way does not, then the admixture of high boiling-point oils containing phenolic bodies with a substance free from phenols (e.g., asphalts, etc.) is established. It is claimed that the presence of as little as 10% of pitch containing phenols may be detected in this manner.

Where bituminous substances contain calcium carbonate, the phenolic bodies present combine with the lime, forming insoluble calcium phenolate which yields but a faint diazo reaction. However, on treating such substances with a solvent in the presence of hydrochloric acid, the calcium phenolate is decomposed, and the diazo reaction becomes much more delicate.

A still more sensitive test for ascertaining the presence of phenols (e.g., tars or pitches) in asphalts consists in the following: A reagent is prepared by dissolving 0.2 g. *p*-nitroaniline in 20 ml. water and 5 ml. 20% sulfuric acid, whereupon 0.3 g. sodium nitrite are added. Hard asphalts (3 to 4 g.) are ground in a mortar with 25 ml. water made alkaline with NaOH; then filtered and the filtrate acidified with H<sub>2</sub>SO<sub>4</sub> and three drops of the foregoing reagent added. The solution is finally made alkaline with NaOH, whereupon the presence of phenols will develop a more or less intense red coloration. It is claimed that the presence of 1% of tar or pitch may thus be detected, inasmuch as a 1:25,000 solution of phenol will produce a blood-red color, and a 1:250,000 solution a pinkish-red color. Pure asphalts, on the other hand, yield a light-yellow color or leave the reagent unchanged.

### ANTHRAQUINONE REACTION

The anthraquinone reaction is used for detecting anthracene in tar products produced at high temperatures, including oil-gas-tar and pitch, water-gas-tar and pitch, and the various coal-tar pitches. This test is therefore valuable for purposes of identification.

The tar or pitch is first subjected to distillation in accordance with the retort method, the ofttake and condensing tube being kept warm to prevent the accumulation of any solid distillate. The distillate passing over between 270° and 355°C. is caught separately and examined for anthracene in the following manner. The fraction is heated until it is thoroughly fluid to secure a uniform sample, and 5 g. weighed out, while hot. After cooling, 10 ml. of absolute ethyl alcohol are added,

the solids allowed to crystallize and the liquid decanted. One to 2 g. of solid substances containing the anthracene are dried on a water bath, transferred to a 500-ml. flask connected with a return condenser, 45 ml. of glacial acetic acid added, and the contents boiled for 2 hours. The following mixture is then added drop by drop through a separatory funnel: 15 g. of anhydrous chromic acid dissolved in 10 ml. of glacial acetic acid, and 10 ml. of water. The boiling is continued for another 2 hours, the flask cooled, and 400 ml. cold water added. This treatment oxidizes the anthracene to anthraquinone, which on cooling separates as a solid mass. This is filtered, washed with hot water, then with a hot 1% solution of caustic soda and again with hot water. The residue of anthraquinone is then dried and its weight multiplied by 0.856 to obtain the corresponding weight of anthracene. From 0.25 to 0.75% of anthracene is found in coal tars, and a correspondingly larger percentage in coal-tar pitches.

A color reaction for establishing the presence of anthracene consists in boiling for 30 to 60 minutes the crystals of anthraquinone (1 part) with zinc dust (2 parts) and 50% NaOH solution (30 parts), whereupon an intense red-colored solution is obtained, which on filtering in contact with air becomes decolorized.

The determination of anthracene in coal-tar oils by chromic acid oxidation has been standardized by the standardization of Tar Products Test Committee under the designation Serial No. C.A. 1-57.

# **PART II**

## **EXAMINATION OF BITUMINOUS SUBSTANCES COMBINED WITH DISCRETE AGGREGATES**

### **PHYSICAL TESTS OF FINISHED PRODUCT**

#### **RESISTANCE TO PLASTIC FLOW**

This method of test is intended for the determination of the resistance to plastic flow of specimens of compressed bituminous mixtures composed of fine aggregate [passing a No. 10 (2000 micron) sieve] and bituminous material. The method is intended for testing mixtures of the hot-mix, hot-laid type in which the bituminous material is tar or asphalt cement, and has been standardized as ASTM D1138-52.

**Apparatus.**—The apparatus shall consist of the following:

(a) **Specimen Molds.**—Cylindrical molds (Fig. 28-20) of specially hardened steel,  $2 \pm 0.001$  in. in inside diameter by  $4\frac{3}{4}$  in. in height, for forming test specimens. A minimum of three such molds is recommended.

(b) **Bottom Plungers.**—Steel plungers (Fig. 28-21), 2 in. in length, machined to provide a clearance of 0.002 in. between plungers and specimen molds, the nominal diameter being  $1.998 \pm 0.001$  in. to serve as bottom plungers for specimen molds. A minimum of three such plungers is recommended.

(c) **Temporary Supports for Specimen Molds.**—Two steel bars, 1 in. square and 3 in. in length.

(d) **Top Plunger.**—A steel plunger (Fig. 28-21),  $4\frac{3}{4}$  in. in length, consisting of a steel bottom cylindrical compression plate screwed to the shaft of the plunger. The compression plate shall be machined to provide a clearance of 0.002 in. between plunger and specimen molds, the nominal diameter being  $1.998 \pm 0.001$  in. and the thickness approximately  $\frac{1}{8}$  in. The plunger shaft shall have at least four curved surfaces  $1.98 \pm 0.001$  in. in diameter, as illustrated in Fig. 28-21. A minimum of three such plungers is recommended.

(e) **Testing Mold and Ring.** *Type 1.*—A cylindrical testing mold (Fig. 28-22),  $2.02 \pm 0.002$  in. in inside diameter for the bottom 1.5 in. of the mold, tapering to a maximum inside diameter of  $2.06 \pm 0.002$  in. at the top, and approximately 3.02 in. in outside diameter. The mold shall be  $4\frac{1}{2}$  in. in height and be made of tool steel. The testing mold shall be equipped with a hardened steel testing ring (Fig. 28-22),  $3.02 \pm 0.005$  in. in outside diameter and  $0.25 \pm 0.01$  in. in thickness, with a circular orifice  $1.75 \pm 0.001$  in. in diameter on one face. This orifice shall have a distinct vertical edge  $\frac{1}{16}$  in. in thickness and  $1.75 \pm 0.001$  in. in diameter, and shall taper to a diameter of approximately 2 in. on the opposite face. A testing ring clamp (Fig. 28-22) shall be provided to hold the testing ring snugly



in a concentric position against the bottom of the testing mold and to serve as a base for the testing mold.

**Type 2 (Alternative).**—This testing mold (Fig. 28-23) shall have the same dimensions as Type 1 and shall, in addition, have a special inner lining of hardened and ground tool steel to reduce wear.

**(f) Testing Machine.**—A testing machine capable of applying a total load of 10,000 pounds at a uniform rate of head or platen movement of 2.4 in. per minute.

**(g) Oven or Hot Plate.**—For the preparation of bituminous mixtures, an oven or hot plate shall be provided for heating aggregates and bituminous materials to a temperature not to exceed 162.8°C. (325°F.). [For tar mixtures, aggregates and tar shall be heated to desired temperatures, not exceeding 107.2°C. (225°F.).] When a hot plate is employed, a metal shield shall be interposed between the hot plate and the material and mixing pans and the specimen molds containing the mixture. A convenient shield can be made by crimping the edges of a sheet of metal so as to provide an air space beneath its surface.

**(h) Mixing Apparatus.**—Suitable apparatus for mixing the aggregate and bituminous material for preparation of test specimens. The use of a cylindrical type of dish and a putty knife as a mixer is suggested, or a power-mixing machine equipped with scraping and mixing blades and a cylindrical bowl may be used.

**(i) Water Bath.**—A metal water bath for use in testing specimens, and for holding the testing mold and ring so that the specimens will be immersed in water during test. Apparatus shall be provided for maintaining the temperature of the water in the bath at a temperature of 60° ± 1°C. (140° ± 1.8°F.).

**(j) Balance.**—A balance having a capacity of 500 g. or more and sensitive to 0.1 g., for weighing the ingredients of the mixture.

**Test Specimens. Preparation of Mixtures.**—For fine-aggregate bituminous mixtures prepared in the laboratory, a sufficient quantity of dry aggregates to produce three test specimens shall be weighed out to the nearest 0.1 g. The aggregates shall be heated in a tared mixing dish to the desired temperature, not exceeding 162.8°C. (325°F.), and mixed thoroughly. The dish containing the aggregate shall be placed on a balance and the desired amount of bituminous material at a suitable temperature not exceeding 162.8°C. (325°F.), as determined by means of a thermometer, shall be added to an accuracy of 0.1 g. [For tar mixtures, the aggregates and tar shall be heated to the desired temperatures, not exceeding 107.2°C. (225°F.).] The materials shall be thoroughly and uniformly mixed and

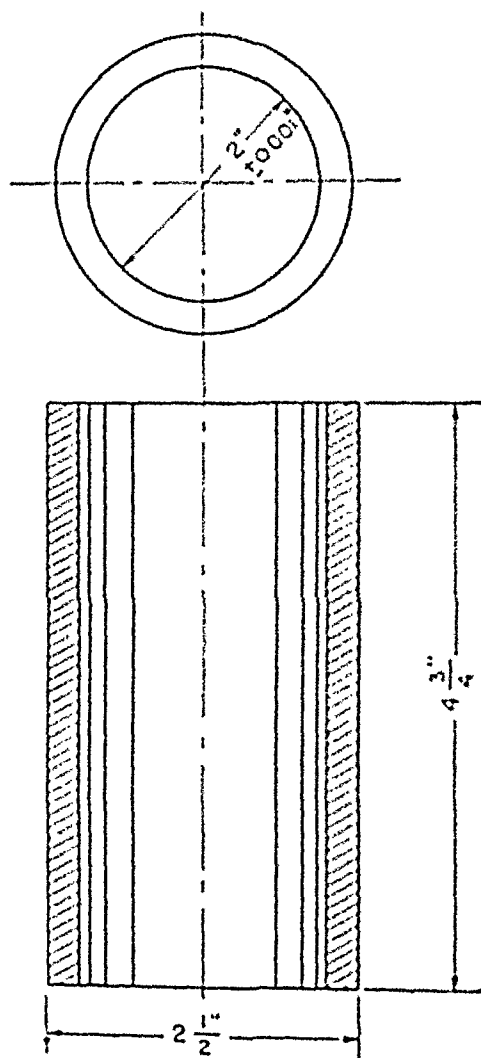


FIG. 28-20. Test Specimen Mold.  
(Courtesy ASTM.)

## 1006 EXAMINATION OF BITUMINOUS SUBSTANCES

all lumps in the mixture shall be broken up. All aggregate surfaces shall be coated and the mixture shall be a uniform color.

**Size of Specimens.**—The test specimens of compressed bituminous mixtures shall be 2 in. in diameter and 1 in. in height. This size of specimen is suitable for

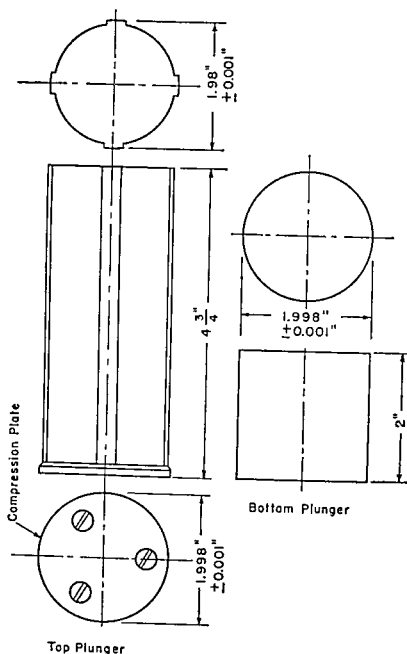


FIG. 28-21. Top and Bottom Plungers. NOTE.—The top and bottom plungers should be machined to provide a clearance of 0.002 in. between plungers and specimen molds, the nominal diameter of the plungers being  $1.998 \pm 0.001$  in. (Courtesy ASTM.)

testing mixtures composed of fine aggregate passing a No. 10 (2000 micron) sieve.

**Molding Specimens in the Laboratory.**—An amount of the freshly prepared or preheated field or laboratory mixture sufficient to give the proper size of compressed specimen shall be placed in each of the three forming molds into which the bottom plungers have previously been inserted. The top plungers shall then be inserted. All of the molds and plungers shall have been preheated to the de-

sired molding temperature before placing any mixture in them. The molds containing the bituminous mixture, with the bottom and top plungers in place, shall be placed in an oven automatically maintained at the desired molding temperature and kept there for 10 minutes or longer to ensure that the desired molding

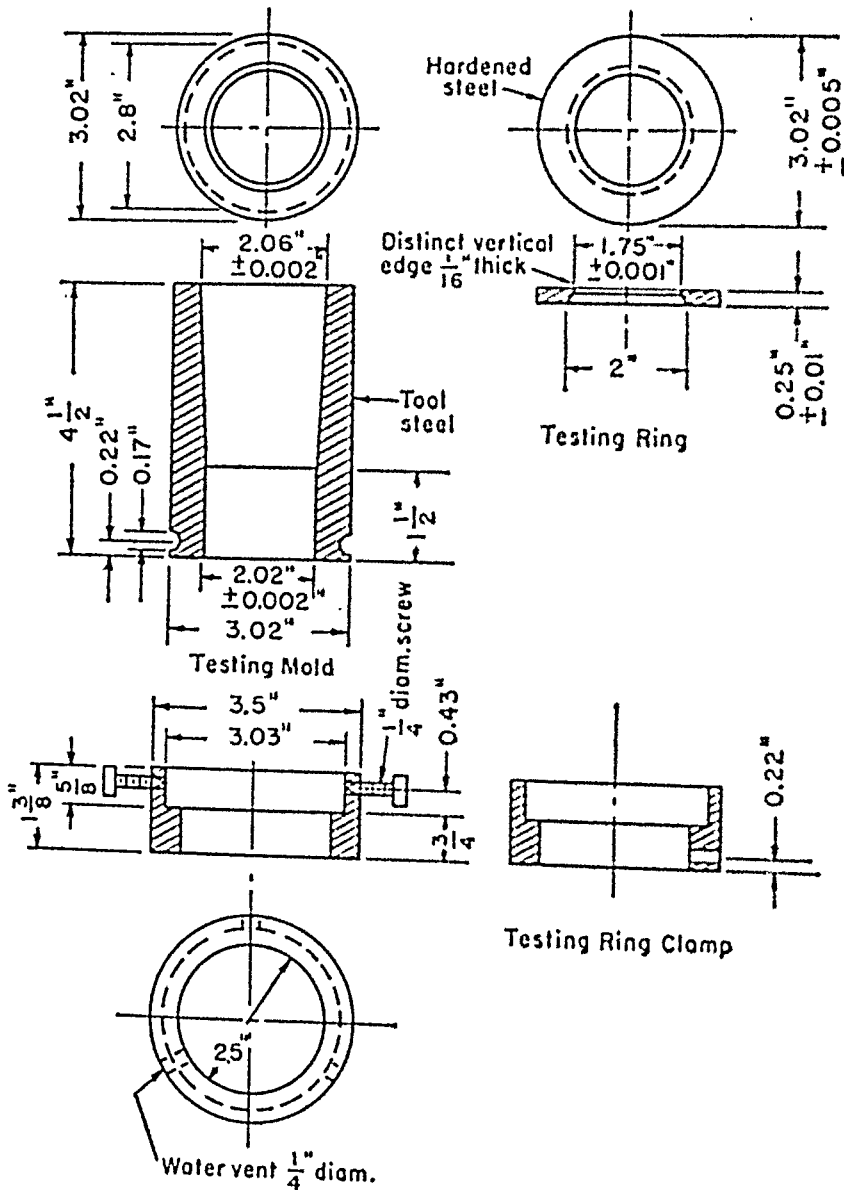


FIG. 28-22. Testing Mold and Ring, Type 1. (Courtesy ASTM.)

temperature has been attained, as determined by means of a thermometer. The top plunger shall be removed from the mold and kept in the oven to retain its temperature during the time the thermometer is inserted in the bituminous mixture in the mold, which should also be kept in the oven. The molding temperature will vary with the type of bituminous binder in the mixture but no temperature higher than 148.9°C. (300°F.) shall be used. [For molding of tar mixtures no temperature higher than 107.2°C. (225°F.) shall be used.] After removal from the oven, the specimens shall be molded with as little delay as possible. The speci-

## PREPARATION OF BITUMINOUS SUBSTANCES

... on the 1-in. square temporary supports so that the bottom of the mold is held at an elevation of 1 in. above the platen of the test machine, thus permitting the bottom plunger to extend only 1 in. into the specimen. An initial load of 500 pounds shall be applied to seat the mix.

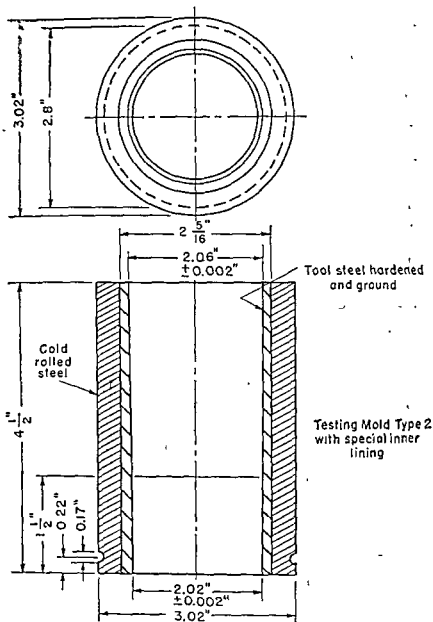


FIG. 28-23. Testing Mold and Ring, Type 2. (Courtesy ASTM.)

ture against the inside of the mold. The initial load then shall be released and the temporary supports removed. The specimen shall be consolidated by applying a pressure of 3000 psi., which corresponds to a total load of 9425 pounds for a specimen 2 in. in diameter. This pressure shall be maintained for 2 minutes and then released. The specimen shall be removed carefully and stored for testing. As short a period of time as possible should be permitted to elapse between the forming of successive specimens.

**Preparation of Core Specimens.**—Cylindrical cores taken from compacted bituminous surfacing shall be  $2 \pm 0.005$  in. in diameter and  $1 \pm 0.05$  in. in height.

**Procedure.**—The test specimen shall be brought to the desired temperature of test by storing in an air bath for at least 1 hour with the temperature of the air maintained at 60°C. (140°F.) during the entire storage period. The testing mold and plunger shall be brought to the test temperature by placing them in the air bath or a suitably controlled water bath for at least 1 hour prior to use.

The test specimen shall be placed in the testing mold, which shall be in the water bath. The temperature of the water in the bath shall be  $60^{\circ} \pm 1^{\circ}\text{C}$ . ( $140^{\circ} \pm 1.8^{\circ}\text{F}$ ). The plunger shall be inserted in the testing mold. Load shall be applied at the uniform rate of head or platen movement of 2.4 in. per minute. As the specimen is loaded it will distort at the orifice of the testing mold, and the load registered on the testing machine will increase quite rapidly to a maximum just before the bond is broken. If the operation is continued, the load will fluctuate below the maximum as flow of the mixture progresses. The maximum load in pounds, registered on the testing machine, shall be recorded as the resistance to plastic flow of the specimen.

**Report.**—The report shall include the following information for each specimen tested:

1. Maximum load in pounds registered on the testing machine during the test, and
2. The test temperature.

## RELATED METHODS

Related methods of testing bituminous mixtures are as follows:

1. *"Method of Testing Soil-Bituminous Mixtures"* (ASTM D915-61).—This method of test provides for the determination of the water absorption, expansion, and extrusion characteristics of compacted soil or soil-aggregate mixtures containing liquid bituminous material (rapid, medium, or slow curing liquid asphalt, emulsified asphalt, or tar). The method may be used for determining the characteristics of a mixture of specified proportions when tested under the conditions of curing or noncuring specified, or for determining the effect on these characteristics of varying the curing and the proportion of the different ingredients. The test results are not intended for use in formulas to determine sub-base, base, or pavement thickness; nor to predict field performance of different bituminous materials.

2. *"Tentative Method of Test for Resistance to Plastic Flow of Bituminous Mixtures by Means of the Marshall Apparatus"* (ASTM D1559-60T).—This method of test is intended for the measurement of the resistance to plastic flow of cylindrical specimens of bituminous paving mixtures loaded on the lateral surface by means of the Marshall apparatus. This method is intended for use with hot mixtures containing asphalt or tar and aggregate up to 1-in. maximum size.

3. *"Tentative Methods of Test for Resistance to Deformation and Cohesion of Bituminous Mixtures by Means of the Hveem Apparatus"* (ASTM D1560-58T).—These methods of test are intended for determining:

(a) The resistance to deformation of compacted bituminous mixtures by measuring the lateral pressure developed from applying a vertical load by means of the Hveem stabilometer.

(b) The cohesion of compacted bituminous mixtures by measuring the force required to break or bend the sample as a cantilever beam by means of the Hveem cohesiometer.

## 1010 EXAMINATION OF BITUMINOUS SUBSTANCES

### 4. "Tentative Methods of Test for Compressive Strength of Bituminous Mixtures" (ASTM D1074-60).

This method of test for compacted bituminous mixtures of the hot-mixed, hot-laid type for use in pavement surfaces and base courses is intended to provide a measure of the compressive strength of these paving mixtures.

### ACCELERATED WEATHERING TEST

This test is intended to produce rapid deterioration of bituminous materials under conditions simulating outdoor exposure and is standardized by the ASTM as "Tentative Recommended Practice for Accelerated Weathering Test of Bituminous Materials" under the designation D529-59T.

Other related tests are "Tentative Method for Preparation of Test Panels for Accelerated and Outdoor Weathering of Bituminous Coatings," ASTM D1669-59T, and "Tentative Method of Test for Failure End Point in Accelerated and Outdoor Weathering of Bituminous Materials," ASTM D1670-59T.

### COAL-TAR PIPE ENAMELS TESTS

Special tests to determine the suitability of coal-tar enamel for coating steel pipe can be found in "AWWA Standard for Coal Tar Enamel Protective Coatings for Steel Water Pipe" (1957) published by the American Water Works Association, Inc., New York.

## SEPARATION OF FINISHED PRODUCT INTO ITS COMPONENT PARTS

### SEPARATION OF THE BITUMINOUS MATTER AND DISCRETE AGGREGATE

Bituminized aggregates are separated into their bituminous and discrete components for the combined purposes of ascertaining the percentage and nature of the mineral constituents and for examining the physical and chemical characteristics of the bituminous binder, with the object of its identification or duplication.

**Hot Extraction with Carbon Disulfide.**—This has been standardized as follows as ASTM D147-41:

Bituminous grouts shall be heated in an oven or on a hot plate in a pan or other suitable container at the lowest possible temperature to prevent overheating and volatilization, and when sufficiently fluid, shall be thoroughly stirred to ensure a uniform sample, whereupon 10 to 30 g. shall be taken for analysis.

Asphalt mastics or mastic cake shall be warmed on a hot plate or in a hot oven until soft enough to be broken up or stirred, so that a representative sample for analysis may be taken. The amount taken for analysis will depend upon the amount of coarse gravel or stone in the mixture. The larger the gravel or stone, the larger will be the sample required for accuracy. The size of samples to be taken shall be as follows: Where all particles pass a No. 10 sieve, 10 to 30 g.; where 25% of the aggregate is retained on a No. 10 sieve, 50 g.; where 50% of the aggregate is retained on a No. 10 sieve, 100 g.; and where 75% of the aggregate is retained on a No. 10 sieve, 200 g.

(a) For Analysis of 10- to 30-g. Samples.—In cases where a 10- to 30-g. sample is sufficient, the analysis shall be carried out by means of the glass extractor illustrated in Fig. 28-24.

An ordinary fat-free Whatman or S. & S. filter thimble, 60 mm. in length by 26 mm. outside diameter, shall be dried for 30 minutes in an oven at 212°F., allowed to cool in a desiccator, and then weighed in a suitable weighing bottle.

The weighed sample shall be placed in the thimble and 40 to 50 ml. of carbon disulfide poured over the sample. The thimble containing the sample shall be suspended under the condenser by a fine wire bail.

The flask shall be cautiously heated by a steam bath or electric heater just enough to vaporize the solvent. Cold water is circulated through the condenser. The heat evaporates the carbon disulfide in the flask. This condenses upon the condenser and drops back upon the sample through which it filters, thus dissolving out the bitumen which collects in the bottom of the flask.

The extraction should be discontinued when the carbon disulfide drops colorless from the filter. The time of extraction will depend upon the nature of the bitumen and mineral aggregate in the sample and upon the degree of heat applied, the coldness of the water in the condenser, and other factors. In some cases extraction may be complete in 1 hour; in others 4 or 5 hours may be necessary.

When the solvent comes through clear, the filter shall be removed and washed with a fine jet of carbon disulfide from a washing bottle to wash out any bitumen that may be retained at the top of the paper and to break up any channels that may have been formed by the carbon disulfide passing through. If the washings show any color, the thimble shall be put back and extraction continued until the solvent again becomes colorless. It shall then be removed, dried carefully, at a low temperature at first to prevent ignition of the absorbed carbon disulfide, and finally to constant weight at 100°C. (212°F.), cooled, and weighed.

An aliquot portion of the solution in the flask shall be rinsed into a weighed porcelain or silica evaporating dish or crucible and the solvent burned off under a hood. The residue shall be ignited over a flame or in a muffle and the ash weighed and the weight added to that of the mineral matter in the filter paper. This is to correct for the fine mineral matter which will be carried through the paper by the solvent. Should there be a considerable amount of ash recovered in this way, and if it is found that the mineral matter is calcium or other carbonate, it shall be recarbonated by repeated treatment with ammonium carbonate solution and finally ignited at a dull red heat. Ordinarily, however, the mineral matter going through the paper will be so small in amount that the difference caused by ignition may be neglected. The corrected loss in weight on the original sample represents the percentage of bitumen present.

The sieve analysis of the recovered mineral aggregate shall be made in accordance with the "Tentative Method of Test for Sieve Analysis of Fine and Coarse Aggregates," ASTM C136-61T.

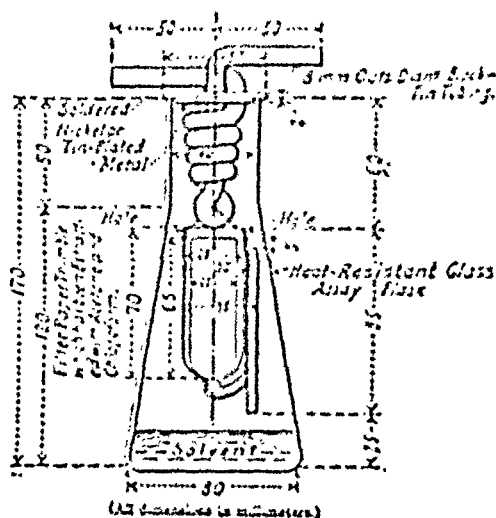
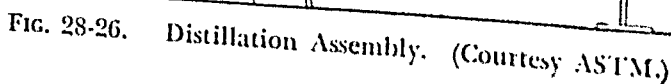
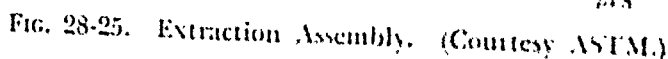


FIG. 28-21. Extraction Apparatus. (Courtesy ASTM.)





(b) **For Analysis of 50- to 500-g. Samples.**—The apparatus for analysis of samples containing coarser aggregate shall be a large extractor consisting of a heat-resistant glass cylinder for holding the solvent and a cylindrical wire basket made of 80-mesh wire cloth suspended in the cylinder from an inverted conical coil condenser which serves as a top. The heat-resistant glass cylinder shall be 13 in. in length with an o.d. of 111 mm. and 4-mm. wall thickness. The wire basket shall be of 80-mesh stainless steel wire cloth with overall length of  $6\frac{1}{4}$  in. and diameter  $2\frac{3}{4}$  in.

A large filter paper, 12 or 13 in. in diameter, shall be fitted inside the wire basket of the extractor by folding once more than in ordinary filtering, or by wrapping it over a form which fits inside the basket (a cylindrical bottle of proper size makes a good form) and placing it inside the basket.

The basket with contained filter paper shall be dried and weighed. The sample shall be weighed and packed in the filter paper in the basket. Care should be taken not to pack all coarse particles in one place and the fine particles in another, but to have them mixed together in uniform proportions.

The sample shall be covered with a disk of felt or wad of absorbent cotton to ensure even distribution of the dropping solvent, thus preventing it from forming a channel through the sample. The basket shall be suspended in the extractor and 150 to 200 ml. of carbon disulfide poured over the felt or cotton. The condenser shall be placed over the top and water circulated through it. The extraction apparatus shall be heated on a steam bath or electric hot plate, and the extraction carried on exactly as in the smaller glass extractor, but on a larger scale. The time for extraction will vary from 3 to 12 hours or more, depending upon the nature of the sample.

To determine when extraction is complete, the condenser shall be raised and the basket lifted out to observe if drippings are clear. One or two drops caught upon white filter paper should leave but a light stain.

The drying and weighing of the basket, burning off of the solution for correction, and calculation of the weight of mineral matter shall be determined as in the foregoing.

The sieve analysis of the recovered aggregate is made in accordance with ASTM C136-61T.

### HOT EXTRACTION WITH BENZENE

Recovery and preparation for test of the bituminous matter soluble in pure benzene shall be made in accordance with the "Standard Method of Test for Hot Extraction of Asphaltic Materials and Recovery of Bitumen by the Modified Albon Procedure," ASTM D762-49. This method is performed as follows:

This method of test covers the procedure for the extraction of benzene soluble bitumen from asphaltic mixtures, the removal of mineral matter from the solution, and the recovery of the bitumen from solution in sufficient quantity for further testing.

**Apparatus.**—The apparatus shall consist of the following:

(a) **Extractor.**—An extraction apparatus as shown in Fig. 28-25.

(b) **Distillation Assembly.**—A distillation assembly as shown in Fig. 28-26 consisting of the following items:

1. A distillation flask as shown in Fig. 28-27.

2. A heat-resistant glass distillation column 250 mm. in length and 25 mm. in



## 1014 EXAMINATION OF BITUMINOUS SUBSTANCES

diameter, and provided with a side arm 150 mm. in length and 8 mm. in diameter.

3. A 250-ml. Erlenmeyer receiving flask and a 250-ml. Erlenmeyer filtering flask.

4. An iron tripod, a 6- by 6-in. 20-mesh wire gauze with an asbestos center, and a gas burner.

5. A water-jacketed condenser 475 to 500 mm. in length.

6. Three thermometers conforming to the requirements for thermometer 7°F-39 as prescribed in the Standard and Specifications for ASTM Thermometers (ASTM E1-61).

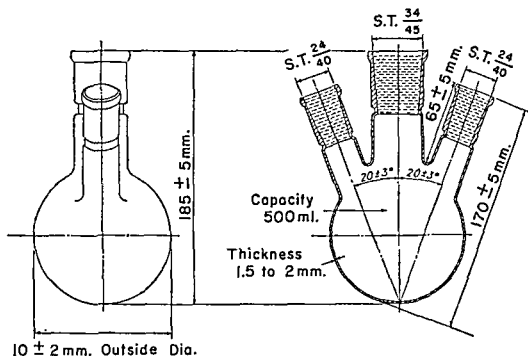


FIG. 28-27. Distillation Flask. (Courtesy ASTM.)

7. A 500-ml. graduated cylinder.

8. A ringstand and supports.

9. An oil bath for the distillation flask.

10. A gas flow meter as shown in Fig. 28-26 or any type capable of indicating a gas flow up to 1000 ml. per minute.

11. A gas inlet tube.

12. A cylindrical, flat-bottom, seamless tin container of 6-ounce capacity. The container shall be 70 mm. (2¾ in.) in diameter and 45 mm. in depth (NOTE).

NOTE.—Containers known in the drug trade as seamless "ointment boxes" may be obtained in the dimensions conforming to these requirements.

**Reagents.**—The reagents needed shall be:

(a) Benzene conforming to the Standard Specifications for Nitration Grade Benzene (ASTM D835).

(b) Carbon Dioxide.

**Sample.**—A sample of sufficient size to result in at least 100 g. of recovered bitumen is required. About 1000 g. of sheet-asphalt mixtures will usually be sufficient unless the largest particles in the sample are 1 in., in which case 2000 g. will usually be necessary. Mixtures containing larger aggregates will require still larger samples.

*Procedure.*—The entire procedure must be completed within 8 hr.

The sample shall be placed in the oven at 210° to 220°F. for 15 minutes, broken into pieces and dried in the oven for an additional 30 minutes. The desired amount of the sample shall be weighed to the nearest 5 g. and placed in the basket of the extractor with the stirrer in place. The extractor shall be charged with 400 ml. of benzene and the wire cone hung on the bottom of the basket. The basket shall be inserted in the extractor, the condenser cover placed on the extractor and the handle placed on the stirrer. Cold water shall be circulated through the condenser. The electric heater shall be connected and the sample extracted until the benzene is colorless (NOTE). The stirrer shall be turned by hand one-half turn every 15 minutes (after the benzene becomes straw colored) to break up any settled filler and remove the last traces of bitumen.

NOTE.—This can be observed by placing a light at one window of the extractor and observing the dripping benzene through the other window.

The benzene solution shall be drawn off and the volume increased to 400 ml. by the addition of fresh benzene, using this solution to wash the extractor if necessary. The solution shall be poured into two 8-ounce wide-mouth bottles, balanced accurately, stoppered, and placed in the centrifuge. The solution shall be centrifuged at room temperature for 30 minutes at 770 times gravity using the distance (in feet) from the center of the centrifuge to a point midway in the liquid as the value of  $R$  in the following formula for calculation of speed of the centrifuge:

$$\text{Speed, r.p.m.} = \frac{1500}{R}$$

The solution shall be poured into a previously weighed 500-ml., three-neck flask, care being taken not to disturb or include the sediment.

Using the distillation assembly shown in Fig. 28-26, the temperature shall be raised inside the flask to 300°F. (148.9°C.) at such a rate that the benzene is collected at a rate of 50 to 70 drops per minute. As soon as this rate falls off, carbon dioxide gas shall be admitted slowly, increasing to a rate of 800 to 900 ml. per minute. The contents of the flask shall be maintained at 295° to 305°F. (146.1° to 151.7°C.) for exactly 30 minutes with full carbon dioxide gas rate. The outside bath temperature ordinarily shall be held 15° to 25°F. (8° to 14°C.) higher than the inside in order to maintain a sample temperature of 295° to 305°F. (146.1° to 151.7°C.).

The flame shall be removed, the carbon dioxide gas shut off, and the apparatus disassembled. The contents of the flask shall then be poured into the 6-ounce container and cooled for further testing.

### CENTRIFUGAL EXTRACTION METHOD

This method is standardized as ASTM D1097-58 under the title of "Standard Method of Test for Bitumen Content of Paving Mixtures by Centrifuge" and is performed as follows:

This method of test is intended for the determination, by cold solvent extraction, of the percentage of bitumen (NOTE) in a paving mixture, the aggregate in which all passes a 1-in. sieve. It is not intended for use in recovering the bitumen for further testing. The mineral matter recovered from this test can be used for sieve analysis.

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**NOTE.**—Although “bitumen” by definition is material soluble in carbon disulfide, benzene is recommended for use in this method for safety reasons, and it normally produces the same results within the precision of the method. Other solvents, such as carbon tetrachloride, trichlorethylene, etc., may be substituted for benzene or carbon disulfide in this method and similar results may be obtained, but the relationship of such results to those obtained with benzene or carbon disulfide cannot be predicted or assumed.

If volatile distillates are desired, they may be obtained by the Method of Test for Moisture or Volatile Distillates in Bituminous Mixtures (ASTM D1461-60).

**Apparatus.**—The apparatus shall consist of the following:

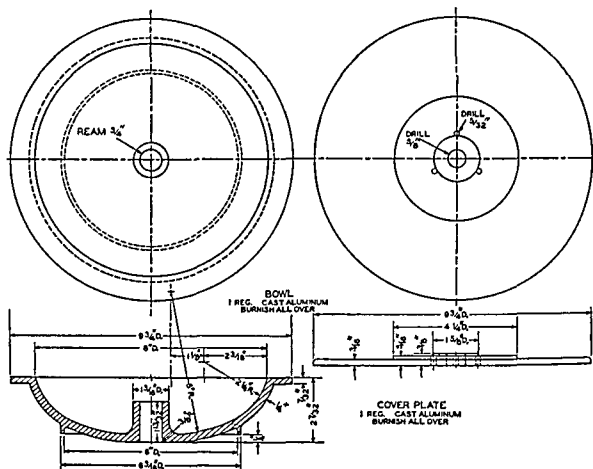


FIG. 28-28. Bowl for Extraction Apparatus. (Courtesy ASTM.)

(a) Extraction apparatus consisting of a bowl approximating that shown in Fig. 28-28 and an apparatus in which the bowl may be revolved at controlled variable speeds up to 3600 r.p.m. The apparatus shall be provided with a shell for catching the solvent thrown from the bowl and a drain for removing the solvent. The apparatus preferably shall be provided with explosion-proof features and installed under a hood to provide ventilation.

(b) Filter rings to fit the rim of the bowl.

**Reagents.** (a) Benzene conforming to the Standard Specifications for Industrial Grade Benzene (ASTM D836).

(b) Ammonium Carbonate Solution.—Prepare a saturated solution of c.p.  $(\text{NH}_4)_2\text{CO}_3$ .

(c) Creosote, crystal-free, conforming to the Standard Specifications for Creosote

for Priming Coat with Coal-Tar Pitch in Dampproofing and Waterproofing (ASTM D43).

**Preparation of Sample.**—(a) If the mixture is not sufficiently soft to separate with a spatula or trowel, place 2000 to 5000 g. of the sample in a large, flat pan and warm in oven at 240°F., only until it can be so handled. Separate the particles of the sample as uniformly as possible, using care not to fracture the mineral particles, and weigh a representative 1000-g. portion into the bowl, distributing it uniformly around the bowl. For routine testing, smaller samples may be used when the maximum size aggregate therein is less than  $\frac{1}{4}$  in. The precision of the method becomes less as the aggregate size increases, due to variations in samples. It may, however, be used on mixtures containing aggregate larger than 1 in. by using samples weighing at least 3000 g. They may be tested by extracting 1000 g. at a time.

(b) Cover the sample in the bowl with benzene and allow sufficient time for the solvent to disintegrate the sample before testing (not more than 1 hour).

(c) At the same time, weigh 500 g. of the sample into a metal still conforming to that used in the Method of Test for Water in Petroleum Products and Other Bituminous Materials (ASTM D95-58).

**Procedure.**—(a) Place the bowl containing the sample and solvent in the machine. Dry and weigh the filter ring and fit it around the edge of the bowl. Clamp the cover over the bowl tightly in place and put the beaker under the drain to collect the extract.

(b) Start the machine revolving slowly, gradually increasing speed to a maximum of 3600 r.p.m., or until solvent ceases to flow from the drain. Allow the machine to stop, add 200 ml. of benzene, and repeat the above procedure. Use sufficient 200-ml. solvent additions (not less than three) so that the extract is clear and not darker than a light-straw color when a portion is viewed in a separate container.

(c) Remove the filter ring from the bowl, dry in air and then to constant weight in an oven at 240°F., and weigh. The increase in weight of this ring during the extraction procedure is mineral matter. Evaporate the contents of the bowl to dryness on the steam bath and then heat in an oven at 240°F. to constant weight after cooling.

(d) Collect all extract in a 2000-ml. graduate and measure the total volume. Agitate the extract thoroughly and measure 100 ml. into a previously weighed ignition dish. Evaporate the extract in the dish to dryness on a steam bath and ash the residue at a dull red heat. Ash the bituminous material at a dull red heat (500° to 600°C.), cool, and add 5 ml. of saturated ammonium carbonate  $(\text{NH}_4)_2\text{CO}_3$  solution per gram of ash. Digest at room temperature for 1 hour and then dry in an oven at 110°C. to constant weight, cool in a desiccator, and weigh. Calculate the weight of ash in the entire volume of extract.

(e) Determine the water content of the sample in the metal still in accordance with ASTM D95-58.

Calculate the percentage bitumen in the sample as follows:

$$\text{Bitumen content of dry sample, \%} = \frac{(W_1 - W_2) - (W_3 + W_4 + W_5)}{W_1 - W_2} \times 100$$

where  $W_1$  = weight of sample

$W_2$  = weight of water in sample

$W_3$  = weight of extracted mineral matter

$W_4$  = weight of ash in extract

$W_5$  = increase in the weight of the filter ring

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**NOTE. Determination of Tar.**—For paving mixtures in which tar is used as the binder, the tar content can be determined by the following modification of this method:

Cover the sample in the bowl with crystal-free creosote and place the bowl for 1 hour on a hot plate or in an oven maintained at 240°F. Proceed in accordance with paragraphs (a) and (b) of the above procedure except to use two 200-ml. additions of creosote previously heated to 240°F. After draining the third portion of hot creosote, allow the bowl and contents to cool to a temperature well below the boiling point of benzene. Treat the sample in the bowl with three 200-ml. additions of benzene, following the same procedure.

Continue in accordance with paragraphs (c) to (e), except to evaporate the aliquot portion of the solvent [see paragraph (d)] on the steam bath until the benzene is removed. Then evaporate the remaining solvent to dryness on a hot plate and ash as directed in paragraph (d).

Calculate the percentage of tar in the sample as described above for percentage of bitumen.

**NOTE. Related Test.**—A related test is ASTM D313-60 "Standard Method of Test for Coarse Particles in Mixtures of Asphalt and Mineral Matter." In this test the sample is dissolved in carbon disulfide, carbon tetrachloride, or benzene and passed through a 200-mesh sieve. This insoluble material remaining on the sieve is then weighed.

# PART III

## EXAMINATION OF BITUMINIZED FABRICS

This section includes the following groups of products:

- Q*—Prepared roofings.
- R*—Composition shingles.
- S*—Deck and porch coverings.
- T*—Bituminized fabrics for constructing built-up roofs.
- U*—Bituminized fabrics for constructing waterproofing membranes.
- V*—Electrical insulating tape.
- W*—Waterproof papers for wrapping and packing.
- X*—Waterproof papers for insulating against heat or cold.
- Y*—Felt-base floor coverings (surfaced with linseed oil and pigment composition).
- Z*—Expansion joints for pavements.

TABLE 28-4

	Paper		Burlap		Duck		Light Cotton Fabric		Rag-Felt		Asbestos Felt		Burlap and Rag or Asbestos Felt		Paper and Light Cotton Fabric	
	<i>a</i>	<i>t</i>	<i>a</i>	<i>t</i>	<i>a</i>	<i>t</i>	<i>a</i>	<i>t</i>	<i>a</i>	<i>t</i>	<i>a</i>	<i>t</i>	<i>a</i>	<i>t</i>	<i>a</i>	<i>t</i>
<i>Single Layered:</i>																
Saturated only.....	<b>WX</b>	<b>WX</b>	<b>U</b>	<b>U</b>	—	—	—	—	<b>TUY</b>	<b>TU</b>	<b>T</b>	—	—	—	—	—
Coated only (one or two sides).....	<b>W</b>	—	<b>U</b>	<b>U</b>	<b>S</b>	—	—	—	—	—	—	—	—	—	—	—
Saturated and coated.....	<b>X</b>	—	<b>U</b>	<b>U</b>	<b>QS</b>	—	<b>V</b>	—	<b>QR</b>	—	<b>Q</b>	—	—	—	—	—
<i>Laminated (Bituminated):</i>																
Layers saturated only.....	—	—	<b>Z</b>	—	—	—	—	—	<b>Z</b>	<b>Q</b>	<b>QT</b>	—	<b>UZ</b>	<b>U</b>	—	—
Layers saturated and coated.....	—	—	—	—	—	—	—	—	<b>Q</b>	—	<b>Q</b>	—	<b>Q</b>	—	—	—
Layers unsaturated.....	<b>W</b>	<b>W</b>	—	—	—	—	—	—	—	—	—	—	—	—	<b>W</b>	<b>W</b>
One layer unsaturated and others saturated.....	<b>W</b>	<b>W</b>	—	—	—	—	—	—	—	—	—	—	—	—	<b>W</b>	<b>W</b>

NOTE.—Letters in heavy type indicate the more important groups of products.

These are constructed as shown in Table 28-4, where the index *a* indicates that asphaltic compositions have been used, and *t* signifies that coal tar (pitch) *et al.*, have been used.



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The finished products falling in this class include sheet roofings, floor coverings, waterproof membranes, sheathing and insulating papers, expansion joints involving the use of woven or felted fabrics, electrical insulating tape, and certain types of wall board. As these are constructed in many different ways, it will obviously be impracticable to describe in detail the analytical methods applicable to each. The ones which follow have been devised specifically for examining prepared roofings, but with these as a starting point, others may readily be evolved for testing floor coverings, waterproof membranes, sheathing and insulating papers, etc.

### FELTED AND WOVEN FABRICS SATURATED WITH BITUMINOUS SUBSTANCES

Methods applicable to saturated felted and woven fabrics have been standardized by the ASTM as "Standard Methods of Sampling and Testing Felted and Woven Fabrics Saturated with Bituminous Substances for Use in Waterproofing and Roofing" under the designation D146-59 as follows:

**Sampling.**—From each shipment of the specified saturated felt or fabric select at random a number of rolls equal to one-half the cube root of the total number of rolls in the lot. The minimum sample shall consist of five rolls. If the calculated number is fractional, express it as the next highest whole number. For convenience, the following tabulation, showing the number of rolls to be selected from shipment of various sizes, is given:

<i>No. of Rolls in Shipment</i>	<i>No. of Rolls in Sample</i>
Up to 1000 . . . . .	5
1001-1728 . . . . .	6
1729-2744 . . . . .	7
2745-4096 . . . . .	8
4097-5832 . . . . .	9
5833-8000 . . . . .	10
8001-10,648 . . . . .	11
10,649-13,842 . . . . .	12
13,843-17,576 . . . . .	13
15,577-21,952 . . . . .	14

The rolls so selected constitute the representative sample used for all subsequent observations and tests pertaining to the lot of material being examined.

**Examination of Sample Rolls.** **Gross Weight per Roll.**—Weigh each roll, intact, to the nearest  $\frac{1}{4}$  pound, and record the weight of each roll as the "gross weight."

**Weight of Wrapping Material and Mandrel.**—Strip each roll of its wrappings and weigh it to the nearest  $\frac{1}{4}$  pound. If mandrels (cores) are used, collect them after the rolls are unwound and weigh them together, to the nearest  $\frac{1}{4}$  pound. Calculate the average weight of wrappings and mandrel per roll, and record as the average weight for the lot.

**Mandrels (Cores).**—Determine the shape of cross-section of mandrels (cores) and report. If circular, measure the outside diameter, to the nearest  $\frac{1}{16}$  in. If square, measure each outside edge to the nearest  $\frac{1}{16}$  in. Measure and report the length of mandrel projecting beyond each end of each roll to the nearest  $\frac{1}{4}$  in.

**Net Weight.**—Subtract the average weight of wrappings and mandrel from the gross weight of each roll and record the result as the net weight for each roll. Calculate the average net weight and record as the average for the lot.

**Appearance and Dimensions of Rolls.**—Unwind the rolls. Observe the workmanship and finish and record pertinent defects. Measure and record the length of each roll to the nearest inch and its width to the nearest  $\frac{1}{16}$  in. Calculate and record the area of material contained in each roll to the nearest square foot.

For fabrics, measure and record the width of the selvage of each roll to the nearest  $\frac{1}{8}$  in.

**Net Weight per Unit Area.**—From the net weight and dimensions, calculate the net weight per unit area for each roll, as follows:

For felts:

$$\text{Net weight, lb. per 100 sq. ft.} = \frac{A}{BC} \times 1200$$

For fabrics:

$$\text{Net weight, oz. per sq. yd.} = \frac{A}{BC} \times 1728$$

where  $A$  = net weight of rolls in pounds

$B$  = width of material in inches

$C$  = length of material in feet

Calculate the average net weight per unit area for the rolls examined and record it as the average for the lot.

**Selecting a Representative Sample.**—Examine in detail the roll having the unit net weight closest to the average unit net weight of the lot. Discard the outside convolution and cut a sample from the full width of the roll. Make the cuts perpendicular to the sides of the roll, straight, and 30 in. apart (to the nearest  $\frac{1}{32}$  in.). Collect loose material, such as sand, if any, that may become detached from the sample. Measure the width of the sample to the nearest  $\frac{1}{16}$  in. Weigh it, together with any detached surfacing, to the nearest gram. Calculate the net weight per unit area, as follows:

For felts:

$$\text{Net weight, lb. per 100 sq. ft.} = 1.0582 \times \frac{D}{E}$$

For fabrics:

$$\text{Net weight, oz. per sq. yd.} = 1.5238 \times \frac{D}{E}$$

where  $D$  = weight of 30-in. sample in grams

$E$  = width of 30-in. sample in inches

The weight so determined should be within 1% of the average net weight per unit area. If the sample so selected fails to conform to this requirement, cut additional samples from the same roll until one of the proper weight is obtained. Use this sample for further examination as described in the following sections.

**Detached Comminuted Surfacing.**—If the material is surfaced with sand or other finely comminuted material, sweep the surfacing from the 30-in. representative sample with a moderately stiff brush. Combine the comminuted material thus removed with the loose material, collected as described in the preceding section.

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and weigh both together to the nearest gram. Calculate this weight in pound per 100 sq. ft., record, and report as detached comminuted surfacing.

**Moisture.**—From the 30-in. representative sample, cut four 2- by 18-in. test specimens as shown at *A-1* and *A-2* in Fig. 28-29. Cut the 2-in. specimens into 1-in. squares and select about 50 g. at random. Weigh to the nearest 0.1 g. and distill with 100 ml. of solvent as prescribed in the Method of Test for Water in Petroleum

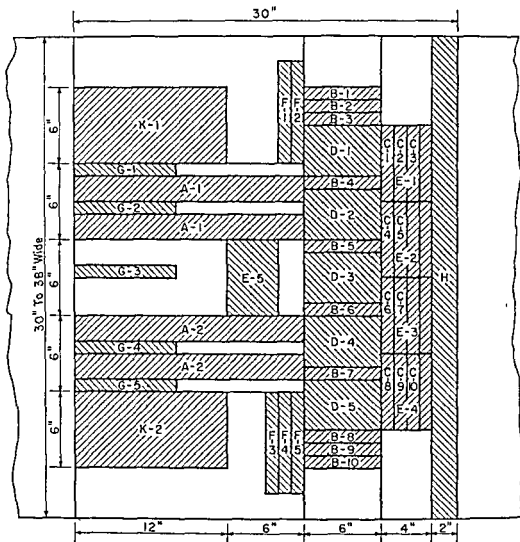


FIG. 28-29. Location of Test Specimens in Sample. (Courtesy ASTM.)

**Products and Other Bituminous Materials (ASTM D95).** Read the volume of water collected in the trap and calculate to grams on the basis that 1 ml. weighs 1 g. Calculate the moisture to the nearest 0.5% of the weight of the sample used (including the detached comminuted surfacing, if any) and report as moisture, percentage of the net weight.

**Strength. Felts.**—From the 30-in. sample cut ten 1- by 6-in. rectangular test strips with the fiber grain, as shown at *B-1* to *B-10* in Fig. 28-29, and ten 1- by 6-in. strips across the fiber grain, as shown at *C-1* to *C-10* in Fig. 28-29. Condition both sets in air at  $77^{\circ} \pm 2^{\circ}\text{F}$ . ( $25.0^{\circ} \pm 1^{\circ}\text{C}$ .) for at least 2 hours, and test in a room maintained at the same temperature. Determine the strength according to the Method

of Test for Tensile Breaking Strength of Paper and Paper Products (ASTM D828), except as modified herein. Cut additional strips from adjacent areas of the 30-in. representative sample when needed because of false breaks. Average the ten readings for each set to the nearest pound, and report as the average breaking strength with and across the fiber grain, respectively.

**Apparatus.**—A tension testing machine is required; it should have the following features.

(a) Two clamps, the jaw edges of which can be set for distances from  $100 \pm 10$  mm. ( $3.94 \pm 0.39$  in.) to  $180 \pm 10$  mm. ( $7.09 \pm 0.39$  in.) apart. The center lines of the clamps should be in the same plane, parallel to the direction of motion, and should be so aligned that they will hold the test specimen in the same plane throughout the test without slippage.

(b) Means of applying a gradually increasing load to the test specimen until it breaks, the rate of increase being such that the additional load applied each second is not different from the additional load applied in the previous second by more than 5%. This condition is fulfilled by the usual pendulum-type apparatus, when the lower clamp moves at a constant rate of speed.

(c) Means of indicating the applied load at the instant of specimen-fracture, to an accuracy of plus or minus 1%.

**Test Specimens.**—(a) The test specimens should be representative of the sample obtained as prescribed in the Standard Method of Sampling Paper and Paper Products ASTM D585.

(b) The specimens should be clean-cut to within plus or minus 1% of their nominal widths, with edges parallel, and should be long enough to be inserted in the jaws of the clamps of the testing apparatus without handling the section under test. Specimens should not exceed 5.08 cm. (2.0 in.) in width and should be not less than 1.27 cm. (0.50 in.) preferably.

**Procedure.**—(a) Level the testing machine and adjust its zero reading. The ratio of the clearance distance between jaws to the width of the specimens should be not less than 5 to 1, nor more than 15 to 1.

(b) After placing the test specimen loosely in the jaws of the clamps, align it squarely, then tighten the upper clamp, take up slack, and finally tighten the lower clamp, without touching the portion of the specimen under test. Then apply the load. Adjust the rate of loading so that the lower clamp moves at a rate of  $12 \pm 0.5$  in. per minute.

(c) Reject readings when the specimen slips in the jaws, or fractures in or at the edge of either jaw.

**Report.**—The report should include the following: (1) results obtained on specimens cut in the machine direction of the paper should be reported as tensile breaking strength, machine direction, and the results obtained on specimens cut in the cross direction of the paper should be reported as tensile breaking strength, cross direction; (2) average, minimum, and maximum values, either as kilograms or as pounds, to three significant figures; (3) number of specimens tested; (4) type and capacity of the apparatus used; (5) rate of loading; (6) specimen width; and (7) distance between jaws of the clamps.

**Reproducibility.**—Duplicate measurements of the tensile breaking strength of different sets of samples from the same lot of paper, and on different apparatus, should agree within 5%.

**Fabrics.**—From the 30-in. sample, cut five 4- by 6-in. test pieces with the longer dimension parallel to the warp yarns, as shown at *D-1* to *D-5* in Fig. 28-29, and

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five pieces with the longer dimension parallel to the filler yarns, as shown at *E-1* to *E-5* in Fig. 28-29. Test these pieces at  $70^{\circ} \pm 2^{\circ}\text{F.}$  ( $21.1^{\circ} \pm 1.1^{\circ}\text{C.}$ ) in accordance with the grab method as described in Section 10 of the General Methods of Testing Woven Fabrics (ASTM D39).

This test is performed as follows:

**Test Specimens.**—Specimens 4 in. in width and not less than 6 in. in length should be taken for test. Two sets of 5 specimens each are required, one set, for warp breaking strength, having the longer dimension parallel to the warp yarns; and the other set, for filling breaking strength, having the longer dimension parallel to the filling yarns. No 2 specimens for warp breaking strength should contain the same warp yarns or, for filling breaking strength, the same filling yarns. Unless otherwise specified, specimens should be taken no nearer the selvage than one-tenth the width of the fabric.

**Testing Machine.**—A tensile testing machine conforming to the requirements of Specifications ASTM D76, should be used. The distance between the clamps at the start of the test should be 3 in. The face of one jaw of each clamp should measure 1 by 1 in., that of the other jaw of each clamp 1 by 2 in. or more, with the longer dimension perpendicular to the direction of application of the load.

**Procedure.**—Place the specimen symmetrically in the clamps of the machine with the longer dimension parallel to and the shorter dimension at right angles to the direction of application of the load, care being taken to grip the same yarns in both clamps. Report the average of the results of the 5 individual tests on the warp as the warp breaking strength, and the average of the 5 individual tests on the filling as the filling breaking strength. If a specimen slips in the clamps, breaks in the clamps, breaks at the edge of the clamps, or, if for any reason attributable to faulty operation, the result falls markedly below the average for the set of specimens, the result should be discarded, another specimen taken, and the result of this break included in the average.

**NOTE.**—As a referee method, or in case any dispute arises regarding the strength, repeat the test, with the exception that the fabric before being tested shall be exposed at least 2 hours in an atmosphere of 65% relative humidity at  $70^{\circ}\text{F.}$  ( $21.1^{\circ}\text{C.}$ ).

**Pliability. Felts.**—From the 30-in. sample cut ten 1- by 8-in. specimens, five in the direction of and five across the fiber grain, as shown at *F-1* to *F-5*, and at *G-1* to *G-5* in Fig. 28-29, respectively. Immerse them in water at  $77^{\circ}\text{F.}$  ( $25^{\circ}\text{C.}$ ) for 10 to 15 minutes; then remove each specimen separately and immediately bend it  $90^{\circ}$  over the rounded edge of a block at a uniform speed in approximately 2 seconds. The block shall be 3 in. square by 2 in. in thickness, with rounded corners of  $\frac{1}{2}$ -in. radius for 15-pound felts, and  $\frac{3}{4}$ -in. radius for 30-pound felts. In bending, hold the specimen tightly against the upper 2-in. face of the block and bend its projecting end over the rounded corner without exerting any strain other than that required to keep the specimen in contact with the block and to avoid kinking. Consider any surface ruptures exceeding  $\frac{1}{8}$  in. in length as failures.

**Fabrics.**—Cut five 1- by 8-in. test specimens in the direction of the warp, as shown at *G-1* to *G-5* in Fig. 28-29. Immerse them in a cooling mixture of ice and water at  $32^{\circ}\text{F.}$  ( $0^{\circ}\text{C.}$ ) for 10 to 15 minutes; then remove each specimen separately and immediately bend it over a  $\frac{1}{16}$ -in. mandrel through an arc of  $180^{\circ}$  at a uniform speed in approximately 2 seconds and then through  $360^{\circ}$  over the same mandrel in the opposite direction. Dry the specimens thoroughly and examine them. If one or more of the test specimens crack, cut ten specimens from another portion of

the sample and repeat the test. If one or more of these specimens crack, consider the material as failing.

**Loss on Heating.**—From the 30-in. sample, cut two 12- by 6-in. specimens at *K-1* and *K-2* in Fig. 28-29. Weigh each specimen to 1 mg. Suspend both 2 in. apart and parallel near the center of an oven maintained at  $221^{\circ} \pm 5^{\circ}\text{F.}$  ( $105^{\circ} \pm 3^{\circ}\text{C.}$ ). Insert a thermometer in the oven to such a depth that its bulb will be in line with the center of the specimens. Keep them in the oven for exactly 5 hours; then remove them carefully and cool and weigh each specimen. Calculate the average loss to the nearest 0.5% of the specimen weights (including the detached comminuted surfacing, if any). Report this figure as the loss on heating. Subtract the percentage of moisture and report as the loss on heating exclusive of moisture.

**Examination of Desaturated Felt or Fabric.** **Weight of Desaturated Felt or Fabric.**—(a) Cut a 2-in. strip ( $\pm \frac{1}{32}$  in.) from across the 30-in. representative sample as shown at *H* in Fig. 28-29. Measure its length to the nearest  $\frac{1}{16}$  in. and calculate its area to the nearest square inch. Extract the test strip as described in the Methods of Testing Bituminous Mastics, Grouts, and Like Mixtures (ASTM D147), except that the strip shall be placed either in the large apparatus described in Section 3(b) of Methods D147-41 or in the large glass extractor shown in Fig. 28-30 of these Methods D146-59. When the drippings have become colorless, dry the extracted specimen in the basket or thimble, first at room temperature in a ventilated fume chamber and then in a ventilated oven at  $221^{\circ} \pm 5^{\circ}\text{F.}$  ( $105^{\circ} \pm 3^{\circ}\text{C.}$ ), and cool in a desiccator. Remove the desaturated felt or fabric, brush off any adherent comminuted surfacing into the filter, and quickly weigh the felt or fabric to the nearest 0.1 mg. Repeat the heating, cooling in desiccator, and weighing of the desaturated felt or fabric to constant weight. From the area of the specimens and the weight of desaturated felt or fabric, calculate the weight per unit area of moisture-free desaturated felt or fabric. Report this weight to the nearest 0.1 pound per 100 sq. ft. for felts and to the nearest  $\frac{1}{2}$  ounce per sq. yd. for fabrics.

(b) Where coal-tar saturant has been used (see following section), correct the moisture-free weight of the desaturated felt or fabric for carbonaceous matter retained mechanically in its interstices by multiplying by  $100 - F/100$ , where *F* is the percentage of retained carbonaceous matter as determined in the following section.

(c) Recover the mineral matter in the filter paper and in the bituminous solution obtained in the extraction of the fabric by the method described in Section (a) of Method D147-41. Determine its weight to the nearest 0.1 mg., calculate to the nearest pound per 100 sq. ft., and record as adherent mineral matter.

**Retained Carbonaceous Matter.**—Determine the carbonaceous matter derived from a coal-tar pitch saturant and retained by the desaturated fabric by means of the following colorimetric method:

(a) Macerate by boiling in water about 15 g. of an unsaturated fabric of the same general character as the one under examination, disintegrate with a rotary egg-beater, and pick the fibers apart with needles. Filter the fibers through fine cloth and dry to constant weight at  $225^{\circ}\text{F.}$  ( $107^{\circ}\text{C.}$ ). Accurately weigh a 1-g. portion of the fiber into a flask and dilute to exactly 100 ml. with distilled water at room temperature. Add about 50 g. of glass beads and shake the contents of the flask vigorously until the fibers are reduced to a homogeneous pulp in uniform suspension.

(b) Procure a distilled coal tar, having approximately 10 to 25% of insoluble carbonaceous matter. Extract the carbonaceous matter with benzene until it is free

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from soluble matter; then dry to constant weight at 225°F. (107°C.). Accurately weigh out a 1-g. portion of the purified carbonaceous matter and dilute to exactly 100 ml. at room temperature with a starch solution of a consistency sufficient to

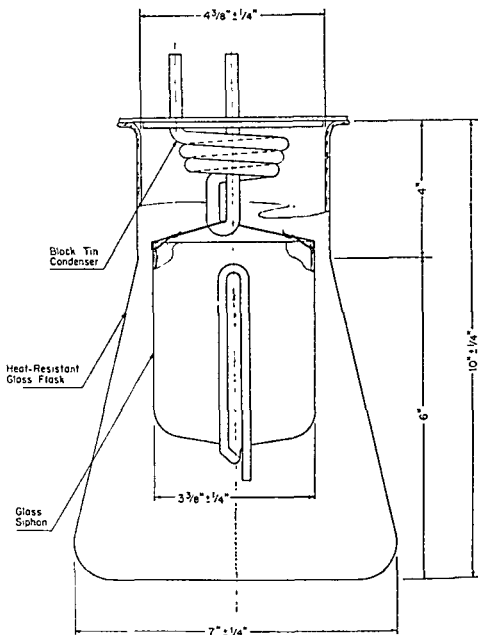


FIG. 28-30. Extraction Apparatus. (Courtesy ASTM.)

carry the carbonaceous matter into temporary suspension. (A 12.5% by weight solution is recommended.)

(c) Titrate the liquid carrying the fibers, obtained as described in paragraph (a), with the suspension of carbonaceous matter, obtained as described in paragraph (b), and examine from time to time a field prepared from a drop of the well-agitated mixture, under a microscope at 100 $\times$  until the color exactly matches a field prepared from the desaturated fabric under examination (obtained as described in the preceding section) when both are viewed side by side under identical condi-

tions. The end point is fairly sharply defined. The buret reading gives directly the percentage of carbonaceous matter adhering to the moisture-free fabric under examination.

**Thread Count of Fabrics.**—Test fabrics for number of threads per inch in accordance with Section 7 of the General Methods of Testing Woven Fabrics (ASTM D39). This is performed as follows:

(a) Number of Ends per Inch.—The actual number of ends (warp yarns or threads) in 1 in. should be counted at 5 or more places in the fabric, and the average number of ends per inch calculated. No 2 spaces counted should include the same yarns. If there are fewer than 25 ends per inch, the ends in 3 in. should be counted at 5 or more different places in the fabric, and the average number of ends per inch calculated. No count should be made nearer the selvage than one-tenth the width of the fabric, nor within 3 yd. of the ends of a roll or bolt. If the fabric is 3 in. or less in width, all the ends should be counted and the result expressed as ends per inch.

(b) Number of Picks per Inch.—The average number of picks (filling yarns or threads) per inch should be determined in accordance with Paragraph (a), above.

**Thickness of Felts.**—Measure the thickness of the desaturated felt at 20 equally spaced spots along the length of the sample strip obtained in paragraph (a) under Weight of Desaturated Felt or Fabric. In all other respects follow Method C of the Methods of Test for Thickness of Paper and Paper Products (ASTM D645). This is performed as follows:

**Apparatus.**—The apparatus should consist essentially of 2 plane parallel faces that can be moved apart or together along an axis perpendicular to themselves. In use, one of these faces (the anvil) should be held stationary, the specimen should be placed over it, and the other face (the presser foot), which is circular, moved towards it until it exerts a predetermined pressure on the specimen. When this condition has been reached, the distance between the 2 faces should be read on a suitable device and recorded as the thickness of the specimen. The presser foot and actuating force should be  $4 \pm 1$  psi.

**Procedure.**—Place the specimen between the jaws of the measuring device and lower the presser foot as gently as possible upon the surface of the paper, with its edge at least  $\frac{1}{4}$  in. from the edge of the paper. Determine the thickness of each of the 10 specimens in each of 2 different places. If the mean between the maximum and minimum of the 20 results differs from the average of all 20 by more than plus or minus 5%, measure enough additional specimens to obtain agreement within these limits.

**Report.**—The report should include the following: (1) method used for determining thickness; (2) relative humidity and temperature of conditioning atmosphere; (3) number of specimens tested, if more or less than 10; (4) width of the specimens, if less than 2 in.; and (5) maximum, minimum, and average thicknesses measured to the nearest 0.0001 in.

**Ash.**—If the weight of desaturated moisture-free felts or fabric is 25 g. or less, ignite the whole desaturated specimen. If it is greater than 25 g., cut the specimen into approximately 1-in. squares, mix them, and select about 25 g. at random for ashing. Dry the ashing sample to constant weight at  $221^{\circ} \pm 5^{\circ}\text{F.}$  ( $105^{\circ} \pm 3^{\circ}\text{C.}$ ). Weigh to the nearest 0.01 g. and ignite in a weighed porcelaine or quartz dish or crucible until all carbon has been consumed. Cool in a desiccator, weigh, and record the weight as ash. Calculate the percentage on the basis of the desaturated moisture-free felt or fabric and report to the nearest 0.1%.



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**Total Comminuted Surfacing.**—Add the weight of adherent mineral matter per 100 sq. ft. to the weight of detached comminuted surfacing per 100 sq. ft., and record as the total comminuted surfacing per 100 sq. ft.

**Bituminous Saturant.**—Determine weight of saturant by subtracting the sum of the weights of the moisture-free desaturated felt or fabric, the moisture, and the total comminuted surfacing, from the weight of the sample, all expressed in pounds per 100 sq. ft. for felts, or ounces per square yard for fabrics. Report these weights, and calculate the ratio of the weight of the saturant to the weight of desaturated moisture-free felt or fabric and report as the ratio of saturant to dry felt or fabric.

### ASPHALT ROLL ROOFING, CAP SHEETS, AND SHINGLES

Methods applicable to roll roofing, cap sheets, and shingles have been standardized by the ASTM as "Tentative Methods of Testing Asphalt Roll Roofing, Cap Sheets, and Shingles" under the designation D228-57T as follows:

**Scope.**—1. These methods cover the procedures for the physical testing and chemical examination of roofing and shingles composed of asphalt-saturated roofing felt coated to various extents with an asphaltic coating and having the coated portion surfaced with mineral powders or granules.

**Types of Roofing and Shingles.**—2. Asphalt roll roofings, cap sheets, and shingles may be divided into three types (see Fig 28-31). Asphaltic coatings on all types may be compounded with mineral stabilizer.

**Type S.**—A single thickness of asphalt-saturated felt, coated with an asphaltic coating, and surfaced, usually on both sides, with fine mineral surfacing such as talc or mica (NOTE).

**NOTE.**—Type S is commercially known as "smooth-surfaced roll roofing" and is covered by the Specifications for Asphalt Roll Roofing Surfaced with Powdered Talc or Mica (ASTM D224-58).

**Type M.**—Similar to type S, but with the asphaltic coating on the weather side surfaced with mineral granules, except for any unsurfaced selvage. The reverse side usually is surfaced with fine mineral surfacing such as talc or mica (NOTE).

**NOTE.**—When in roll form, type M is commercially known as "mineral-surfaced roll roofing" and is covered by the Specifications for Asphalt Roll Roofing Surfaced with Mineral Granules (ASTM D249-55), or, when cut into slabs or shingles, it is commercially known as "asphalt shingles" and is covered by the Specifications for Asphalt Shingles Surfaced with Mineral Granules (ASTM D225-55).

**Type MC.**—Similar to type M, but coated on the weather side for approximately one-half of its width with an asphaltic coating and the coated portion surfaced with mineral granules (NOTE).

**NOTE.**—Type MC is commercially known as "mineral-surfaced cap sheet" and is covered by the Specifications for Wide Selvage Asphalt Roll Roofing Surfaced with Mineral Granules (ASTM D371-55).

**Sampling.**—3. (a) From each shipment or fraction thereof representing a product of the same kind, class, and weight, select at random a number of rolls or bundles equivalent to one-half the cube root of the total number of rolls or bundles included in the lot, except that in lots of 1000 or less, five rolls or bundles shall be taken. If one-half the cube root, as calculated, proves to be a fractional number, express it as the next higher whole number. Table 28-5 shows the number of rolls or bundles to be selected from shipments of various sizes.

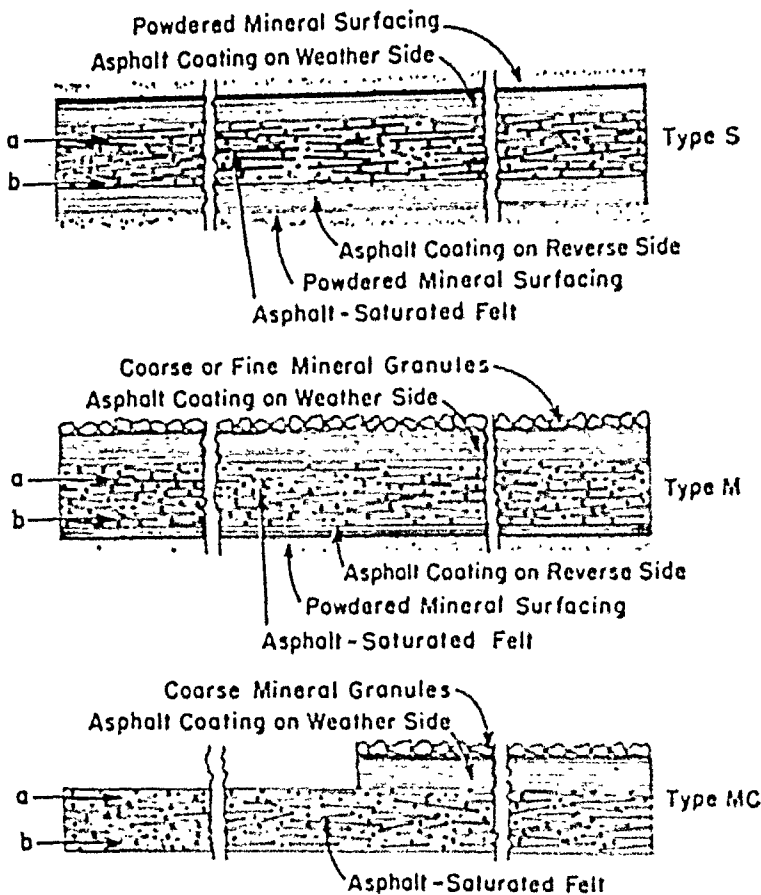


FIG. 28-31. Construction of Asphalt Roll Roofing, Cap Sheets, and Shingles. (Courtesy ASTM.)

TABLE 28-5. NUMBER OF PACKAGES TO BE SELECTED AS SAMPLES

Packages in Shipment	No. of Packages Selected
Up to 1000.....	5
1001 to 1728.....	6
1729 to 2744.....	7
2745 to 4096.....	8
4097 to 5832.....	9
5833 to 8000.....	10
8001 to 10648.....	11
10,649 to 13,824.....	12
13,825 to 17,576.....	13
17,577 to 21,952.....	14

(b) The rolls or bundles selected in accordance with paragraph (a) constitute the representative sample used for all subsequent observations and tests pertaining to the lot of material being examined.

### METHODS OF PHYSICAL TESTING

**Asphalt Roll Roofing and Cap Sheets.** Weight of Roll, and of Packaging Material, Nails, and Cement.—4. Weigh each roll selected in accordance with Section 3, intact, to the nearest  $\frac{1}{4}$  pound, and record the weight of each roll. Weigh the wrappers, packaging material, nails, and cement from each roll to the nearest  $\frac{1}{4}$  pound and record the average weight thereof per roll. Record the quantity and size of nails and presence and character of coating, if any. Record quantity of cement, and whether or not it contains asbestos. Determine the Tag closed flash point in accordance with the Method of Test for Flash Point by Tag Closed Tester (ASTM D56).

**Weight of Loose Surfacing.**—5. Unwind each roll and observe and record the workmanship and finish of the roofing. If any loose surfacing is noted, shake it off, reweigh the roll, and record the loss of weight.

**Width, Length, and Area.**—6. (a) Measure the length and width of the roofing in each roll to the nearest  $\frac{1}{4}$  in., and calculate its area in square feet. From these values calculate the average area of the rolls examined.

(b) Measure the width of selvage to the nearest  $\frac{1}{8}$  in. and note its character.

**Minimum Net Weight per 100 Sq. Ft.**—7. Calculate the net weight per 100 sq. ft. of roofing, exclusive of loose surfacing, contained in each roll. Record the minimum net weight per 100 sq. ft. of the rolls examined as the minimum for the lot.

**Average Net Weight per 100 Sq. Ft.**—8. Calculate the average net weight per 100 sq. ft. for the rolls examined and record as the average net weight in pounds per 100 sq. ft. of the lot.

**Weight per Unit Area and Selection of Representative Sample.**—9. (a) From the rolls examined, select the one whose net weight per 100 sq. ft. is nearest the average of the lot. Lay the selected roll flat, carefully unwind the first one or two convolutions and with a knife and straightedge cut the sheet cleanly across at right angles to the edges. Discard this material, and then take a sample measuring  $30 \pm \frac{1}{2}$  in. in the direction of the length of the roll. Determine the weight of the sample in ounces to the nearest  $\frac{1}{4}$  ounce, neglecting any loose surfacing, and calculate the weight per 100 sq. ft. as follows:

$$\text{Weight, lb. per 100 sq. ft.} = A \times 0.833$$

where  $A$  = weight of 30-in. sample in ounces

0.833 = factor for converting ounces per measured unit area (30 in.  $\times$  36 in.) to pounds per 100 sq. ft.

The weight so determined should be within 1.5% of the average net weight per 100 sq. ft. of the lot (Section 8). If the sample selected fails to conform to this requirement, cut additional samples from the same roll until one of proper weight is obtained. Use this sample for the further examination as described in Sections 16 to 25.

(b) Having selected a sample representative of the lot, trim off any selvage area and weigh the remaining surfaced area in ounces to the nearest  $\frac{1}{4}$  ounce. Calculate the weight per 100 sq. ft. for the surfaced area as follows:

$$\text{Weight of surfaced area, lb. per 100 sq. ft.} = \frac{B}{C} \times 30$$

where  $B$  = weight of 30-in. sample of surfaced area, in ounces

$C$  = width of 30-in. sample, measured at right angles to the length of the roll in inches

30 = factor for converting ounces per measured unit area ( $30 \text{ in} \times C$ ) to pounds per 100 sq. ft.

Record the weight so determined as the average weight per 100 sq. ft. of surfaced area for the lot (NOTE).

NOTE.—As a referee method, or in case any dispute arises regarding the results obtained on the sample selected and tested in accordance with paragraphs (a) and (b), take a 30-in. sample from each roll selected in accordance with Section 3 and examine separately.

**Asphalt Shingles. Weight of Bundle and of Packaging Material.**—10. Weigh each bundle selected in accordance with Section 3 to the nearest  $\frac{1}{4}$  pound and record the weight of each bundle. Weigh the packaging materials from each bundle to the nearest  $\frac{1}{4}$  pound and record the average weight thereof per bundle.

**Weight of Loose Surfacing.**—11. Separate the shingles and observe and record the workmanship and finish. Shake off any loose surfacing, reweigh the bundle, and record the loss in weight and the resultant net weight  $d$  of roofing per bundle.

**Shingle Count and Area.**—12. Count the number of shingles  $e$  in each bundle. Accurately measure two representative shingles to the nearest  $\frac{1}{32}$  in. and determine the net area  $f$  in square feet of material per shingle.

**Minimum Net Weight per 100 Sq. Ft.**—13. Calculate the net weight of roofing material per 100 sq. ft. contained in each bundle as follows:

$$\text{Net weight, lb.} = \frac{d}{e \times f} \times 100$$

where  $d$  = the resultant net weight of roofing per bundle

$e$  = the number of shingles

$f$  = the net area of material per shingle, in square feet

Record the minimum weight per 100 sq. ft. so obtained as the minimum weight per 100 sq. ft. of the lot.

**Average Net Weight per 100 Sq. Ft.**—14. Calculate the average net weight  $g$  per 100 sq. ft. for the bundles examined and record this as the average net weight per 100 sq. ft. of the lot.

Calculate the average net weight per shingle  $(f \times g)/100$ .

**Selection of Representative Samples.**—15. From the bundles examined, set aside for further examination in accordance with Section 17 to 26 a number of representative shingles whose weight falls within 1.5% of the average weight per shingle (Section 14). The total area of the shingles so selected should be as close as possible to 6 sq. ft. of material, and the shingles should be selected from as many different bundles as possible (NOTE 5).

NOTE 5.—As a referee method, or in case any dispute arises regarding the results obtained on the sample selected and tested in accordance with this section, take additional shingles totaling about 6 sq. ft. of material from each bundle selected in accordance with Section 3 and examine separately.

## 1032 EXAMINATION OF BITUMINOUS SUBSTANCES

**Asphalt Roll Roofing and Cap Sheets. Pliability.**—16. From the sample selected in accordance with Section 9, cut ten test specimens 1 in. in width by 8 in. in length, five in the direction of and five across the length of the roll. Immerse in water at 77°F. (25°C.) for 25 to 30 minutes; then remove and immediately bend each specimen, with the weather side up, at a uniform speed through 90° in approximately 2 seconds over the rounded edge of a block. The block shall be 3 in. square by 2 in. thick with rounded corners of  $\frac{1}{2}$ -in. radius for type S roofing and  $\frac{3}{4}$  in. for types M and MC roofing. When bending, hold the specimens by hand tightly against the upper 2-in. face of the block, and bend the projecting end of the specimen over the rounded corner without exerting any strain other than that required to keep the specimen in contact with the block and to avoid kinking. Any surface rupture exceeding  $\frac{1}{8}$  in. in length is considered a failure. Report the number of specimens failing.

**Asphalt Roll Roofing, Cap Sheets, and Shingles. Loss and Behavior on Heating.**—17. Cut two test specimens, each approximately 4 by 4 in., from the sample selected in accordance with Section 9 in the case of asphalt roll roofing and cap sheets, and from the sample selected in accordance with Section 15 in the case of shingles. Condition specimens for 24 hours in a desiccator, weigh, and then by means of a thin wire fastened through holes punctured near one edge, suspend them vertically in the center of an air oven maintained at  $176^{\circ} \pm 5^{\circ}\text{F.}$  ( $80^{\circ} \pm 3^{\circ}\text{C.}$ ) in the same direction as the material would be applied to the roof. The internal dimensions of the oven shall be not less than 12 by 12 by 12 in. The oven shall be electrically heated with forced draft. Insert a thermometer in the center of the oven to such a depth that its bulb is in line with the center of the specimens. Maintain the specimens at the prescribed temperature for exactly 2 hours, then cool in a desiccator and weigh each specimen. Calculate the average loss of volatile matter as percentage of the original specimen weight. Record any change in appearance of the specimen such as blistering, absorption of the asphalt coatings, or sliding of coating or granular surfacing. Record the extent of the latter in inches.

### METHODS OF ANALYSIS

**Composition.**—18. Analyze the representative samples selected in accordance with Sections 9 and 15 for the weights in pounds per 100 sq. ft. of the following components as described in Sections 19 to 25:

Dry felt

Saturant (soluble in carbon disulfide)

Weather side (NOTE) coating (soluble in carbon disulfide)

Reverse side coating (soluble in carbon disulfide)

Mineral surfacing on weather side (NOTE) [passing a No. 6 (3360 micron) sieve and retained on a No. 100 (149 micron) sieve]

Mineral surfacing on reverse side [passing a No. 6 (3360 micron) sieve and retained on a No. 100 (149 micron) sieve]

Mineral matter on weather side (NOTE) [passing a No. 100 (149 micron) sieve], and

Mineral matter on reverse side [passing a No. 100 (149 micron) sieve]

NOTE.—Weather side may be either side on type S roll roofing.

**Selection of Specimens for Analysis.** 19. (a) **Materials of Uniform Thickness.**—From the sample representing the average net weight of the lot of roofing, as obtained in Section 9 or in Section 15, cut test specimens 4 by 4 in. in dimension. Measure specimens to nearest  $\frac{1}{32}$  in., and calculate the area. Weigh these specimens and calculate the weight in pounds per 100 sq. ft. Reject any of the specimens whose weight per 100 sq. ft. varies more than 1.5% from the average net weight as determined in Section 9 or in Section 14. Continue this process until four acceptable specimens are obtained for use in determining the composition of the roofing as described in Sections 21 to 25.

(b) **Heavy Butt Shingles.**—Cut four 4- by 4-in. specimens from the center of the exposed portion of the shingles. Analyze these specimens in accordance with the procedures described in Sections 21 to 25.

Cut four 4- by 4-in. specimens from the center of the exposed portion of the shingles. Analyze these specimens in accordance with the procedures described in Sections 21 to 25.

NOTE.—These methods are not applicable to tapered shingles

**Preparation of Specimens for Analysis.**—20. (a) Warm two of each group of four specimens cut as described in Section 19, for a period not longer than 5 minutes at a temperature of not more than 150°F. (66°C.), and with a sharp knife or spatula separate them into three horizontal sections at approximately the points indicated by the arrows *a* and *b* in Fig. 28-31. Remove the asphalt coatings with attached mineral surfacings in such a manner that a thin but continuous layer of saturated felt adheres to them, thereby obtaining a central section of saturated felt free from coating.

(b) By a similar procedure, split the other two specimens from each group along the mid-line so that each half has approximately one-half of the felt adhering to it. Add any detached mineral surfacing to the section to which it belongs (NOTE).

NOTE.—The specimens may be cut into smaller pieces to facilitate these splitting operations.

**Saturant in Felt.**—21. Dry the saturated central sections from the two test specimens [Section 20(a)] in a desiccator for 2 hours, weigh, and extract with carbon disulfide in a suitable extractor or centrifuge until the washings are colorless. Dry the desaturated felt in air; then place in a tared weighing bottle, dry further at 221° to 230°F. (105° to 110°C.) for 30 minutes, cool in a desiccator, and weigh. Ash the extracted felt as described in Section 24.

**Weight of Weather Side Coating Soluble in Carbon Disulfide.**—22. (a) Weigh and extract the two horizontal sections [Section 20(b)] of the weather side containing the asphalt coating and mineral surfacing (which may be either side on type S roofing) with carbon disulfide in a suitable extractor or centrifuge until the washings are colorless. Remove the pieces of felt and permit them to dry.

(b) Brush the dry felts free of adhering mineral matter, dry in a tared weighing bottle at 221° to 230°F. (105° to 110°C.) for 30 minutes, cool in a desiccator, and weigh. Ash the extracted felts and correct the felt weight for excess mineral matter (Section 24).

(c) Filter the extract and combine the insoluble material so obtained with that brushed from the felts. Dry the combined insolubles in air and then in a tared weighing bottle at 221° to 230°F. (105° to 110°C.) for 30 minutes. Cool in a desiccator and weigh. Save for sieve analysis (Section 25).

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**Weight of Reverse Side Coating Soluble in Carbon Disulfide.**—23. Weigh and extract the two horizontal sections [Section 20(b)] of the reverse side containing the coating and mineral surfacing (which on type S roofing will be the side opposite to that selected under Section 22) as described in Section 22. Determine the dry felt weight, weight of asphalt, and weight of combined mineral matter as described in Section 22. Cool the mineral matter in a desiccator and save for sieve analysis (Section 25) (NOTE).

NOTE.—Other solvents may be used in place of carbon disulfide (Sections 21, 22, and 23) if desired, but the same results may or may not be obtained. In case of dispute, use carbon disulfide.

**Ash of Desaturated Felt.**—24. (a) Ash the desaturated felts obtained in Sections 21, 22, and 23 from the center, weather, and reverse sides separately in tared crucibles, either over an open flame or in a muffle furnace, until all carbon has been consumed. After cooling, add to each ash approximately five times its weight of saturated ammonium carbonate solution, let digest for 1 hour at room temperature in a covered beaker or crucible, dry in an oven at 221° to 230°F. (105° to 110°C.) to constant weight, and record that weight as "ash."

(b) The percentage of ash in the center portion (Section 21) is assumed to be the true percentage of ash of the felt. The difference between this ash and the percentage of ash of the felts recovered in Sections 22 and 23 is presumed to be occluded mineral matter from the coating. This percentage difference is converted to weight and added to the weight of mineral matter passing the No. 100 (149 micron) sieve. The corresponding correction is made to the weight of extracted felt from extraction of weather and reverse sides.

**Weight of Mineral Matter.**—25. (a) Moisten the mineral matter recovered in Section 22 with a few drops of ethyl alcohol, boil with 100 ml. of water, and wash successively through No. 6 (3360 micron) and No. 100 (149 micron) sieves with sufficient hot water to remove the fine mineral matter. Collect the mineral matter retained on each sieve separately, dry at 221° to 230°F. (105° to 110°C.) for 30 minutes, and weigh. To the weight of mineral matter passing the No. 100 sieve, add the weight of excess ash determined in accordance with Section 24. Record as follows:

Passing Sieve	Retained on Sieve	Weight of Mineral Matter
No. 6 (3360 micron) . . . .	No. 6	Record if any
No. 100 (149 micron) . . . .	No. 100	V
(by difference) . . . . .	—	W

In like manner, make similar determinations for the mineral matter recovered in accordance with Section 23.

(b) To check the weight of mineral matter passing a No. 100 (149 micron) sieve, the total aqueous suspension that passes through the No. 100 sieve may be filtered

through a weighed Gooch crucible, dried at 221° to 230°F. (105° to 110°C.), and weighed.

Calculations.—26. Calculate the required values as follows:

$$\text{Ash in felt, \%} = L = \frac{K}{J} \times 100$$

where  $K$  = weight of ash from felt, in grams (Section 21)

$J$  = weight of extracted felt, in grams (Section 21)

$$\text{Saturant in felt, \%} = M = \frac{H - J}{J} \times 100$$

where  $H$  = weight of saturated felt sample, in grams (Section 21).

$$\text{Net weight of felt (NOTE 10), g.} = T = \frac{P(100 - R)}{100 - L}$$

where  $P$  = weight of extracted felt, in grams [Section 22(c)]

$R$  = percentage of total ash in felt (after recarbonation) (Section 24)

$$\text{Trapped mineral matter in felt, g} = P - T$$

Total weight of loose mineral matter in sample (excluding ash inherent in felt), g. =  $Q + (P - T)$

$$\text{Asphalt saturant, g.} = T \times M$$

$$\text{Asphalt coating, g.} = U = N - (P + Q + (T \times M) + (P - T))$$

where  $U$  = weight of the asphalt coating on felt soluble in  $\text{CS}_2$ , in grams (Section 22)

$N$  = weight of the coated sample, in grams (Section 23)

$$\text{Weight of dry felt, lb. per 100 sq. ft.} = \frac{T}{S} \times 31.75$$

where  $S$  = area of the sample, in square inches.

$$\text{Saturant, lb. per 100 sq. ft.} = \frac{T}{S} \times M \times 31.75$$

$$\text{Coating (including mineral stabilizer if any), lb. per 100 sq. ft.} = \frac{U + W}{S} \times 31.75$$

where  $W$  = weight of the mineral matter passing the No. 100 (149 micron) sieve [Section 25(b)].

Mineral matter passing No. 6 and retained on No. 100 sieve, lb. per 100 sq. ft.

$$= \frac{V}{S} \times 31.75$$

where  $V$  = weight of the mineral matter passing the No. 6 (3360 micron) sieve [Section 25(a)].

$$\text{Mineral matter passing No. 100 sieve, lb. per 100 sq. ft.} = \frac{W}{S} \times 31.75$$

$$\text{Mineral matter in coating, \%} = \frac{W}{U + W} \times 100$$



TABLE 28-6 (Continued)

EXAMINATION	
Workmanship.....	smooth, rough, loose, etc. _____
Loss of surfacing per bundle.....	lb. _____
Net weight each bundle.....	lb. _____
Loss on heating.....	per cent _____
Behavior on heating.....	comments _____
	inches sliding _____
Net weight per 100 sq. ft.:	
Average.....	lb. _____
Minimum.....	lb. _____

COMPOSITION	
	Results in lb. per 100 sq. ft.
<i>All Products:</i>	
Dry felt.....	_____
Saturant.....	_____
Weather side coating.....	_____
Reverse side coating.....	_____
Mineral surfacing on weather side.....	_____
Mineral surfacing on reverse side.....	_____
	Results Expressed as Per- centage by Weight
Saturant in felt.....	_____
Mineral matter in coating.....	_____

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NOTE.—In calculating, make the net weight of felt, *T*, equal the sum of the felts recovered from weather and reverse sides. Coating is calculated on the basis of individual analyses of the sections and reported as "weather side" or "reverse side" coating, including stabilizer, if any. Mineral matter may be reported either as total or as from "weather side" or "reverse side." The sieve size should always be reported as determined.

The value 31.75 is the factor for converting weight, in grams, of specimens having the area, *s*, in square inches, to pounds per 100 sq. ft.

Report.—27. The results of a complete examination of the materials tested shall be reported as indicated in Table 28-6.

NOTE.—Methods applicable to asphalt siding have been standardized by the ASTM as "Standard Methods of Testing Asphalt Insulating Siding Surfaced with Mineral Granules" under the designation D1228-58.

TABLE 28-6. REPORT FORM FOR RESULTS

EXAMINATION	
<i>Roll Roofing and Cap Sheets—Types S, M, and MC:</i>	
Weight of each roll. . . . .	lb. _____
Average weight of wrapper, packing material, nails, and cement, total per roll. . . .	lb. _____
Workmanship. . . . .	note any poor condition of rolls such as loose winding and any poor condition of surface of roofing such as rough, loose surfacing material, etc. _____
Selvage. . . . .	width and character _____
Loss of surfacing. . . . .	lb. per roll _____
Pliability. . . . .	number of specimens failing _____
Loss on heating. . . . .	per cent _____
Behavior on heating. . . . .	comments _____
	inches sliding _____
Nails. . . . .	number per roll _____
	size _____
	coating _____
Cement. . . . .	quantity per roll _____
	asbestos _____
	Tag closed flash, deg. Fahr. _____
Net weight per 100 sq. ft.:	
Average. . . . .	lb. _____
Minimum. . . . .	lb. _____
Surfaced sample tested. . . . .	lb. _____
<i>Shingles—Type M:</i>	
Weight of each bundle selected. . . . .	lb. _____
Average weight of packing material per bundle. . . . .	lb. _____
Shingles per bundle. . . . .	number _____
Size of shingle. . . . .	in. _____
Area per shingle. . . . .	sq. ft. _____
Shape. . . . .	describe or sketch _____

TABLE 28-6 (Continued)

EXAMINATION	
Workmanship.....	smooth, rough, loose, etc. _____
Loss of surfacing per bundle.....	lb. _____
Net weight each bundle.....	lb. _____
Loss on heating.....	per cent _____
Behavior on heating.....	comments _____
	inches sliding _____
Net weight per 100 sq. ft.:	
Average.....	lb. _____
Minimum.....	lb. _____
COMPOSITION	
	Results in lb. per 100 sq. ft.
<i>All Products:</i>	
Dry felt.....	_____
Saturant.....	_____
Weather side coating.....	_____
Reverse side coating.....	_____
Mineral surfacing on weather side.....	_____
Mineral surfacing on reverse side.....	_____
	Results Expressed as Per- centage by Weight
Saturant in felt.....	_____
Mineral matter in coating.....	_____

# **PART IV**

## **EXAMINATION OF BITUMINOUS- SOLVENT COMPOSITIONS**

### **PHYSICAL TESTS OF FINISHED PRODUCT**

The following tests have been proposed, concerning which the particulars will be found elsewhere.

Specific Gravity	Color
Viscosity	Gloss
Plasticity and Mobility	Hardness, Abrasion and Adhesion
Flash Point	Water Absorption
Spreading Capacity and Workability	Resistance to Heat
Draining Test	Resistance to Oil
Time of Drying	Resistance to Acids and Alkalies
Hiding Power	Dielectric Strength

### **SEPARATION OF FINISHED PRODUCT INTO ITS COMPONENT PARTS**

#### **RECOVERY OF THE SOLVENT**

*Steam Distillation Method.*—This has been standardized as follows as ASTM D255-61:

The bituminous mixture is distilled in a current of steam, and the solvent is condensed and separated from the water. The steam generator shall be made of either metal or glass, with a capacity of from 2 to 4 l., suitable for continued use in the production of steam. If of glass, it shall be fitted with two outlets with suitable connections for rubber tubing. In the case of a metal generator, a large opening for filling and a water gauge shall be additional parts of the apparatus. The generator shall be supplied with suitable pinch cocks or valves so that steam may be blown off to the atmosphere until the test is ready. The bath shall be of metal of sufficient capacity to permit immersion of the distilling flask to a depth of not less than 10 cm. Heat for the steam generator shall be supplied by a suitable gas generator or electric hot plate. The bath may be heated by any convenient means.

The distilling flask shall be a short ring-neck, round-bottom flask of 1000-ml. capacity. It shall be fitted with a three-hole rubber stopper, a steam distilling tube which will reach to within  $\frac{1}{2}$  in. (12.7 mm.) of the bottom of the flask and project from the top at a convenient distance for connection to the generator, a

vapor outlet tube which extends from beneath the rubber stopper to a point sufficiently above the distilling flask that will permit convenient connection to the condenser, and a thermometer (ASTM 7°C. or 7°F.). The steam tubing should be not less than 2 nor more than 4 mm. in internal diameter and the vapor outlet tube should be not less than 5 mm. in internal diameter.

The condenser shall consist of a  $\frac{3}{16}$ -in. (14.29 mm.) outside diameter No. 20 Stubbs' Gauge seamless brass tube, 22 in. (55.88 cm.) long. It shall be set at an angle of 75° from the perpendicular and be surrounded with a cooling bath 15 in. (38.1 cm.) long, approximately 4 in. (10.16 cm.) wide by 6 in. (15.24 cm.) high. The lower end of the condenser tube shall be cut off at an acute angle, and curved downward for a length of 3 in. (7.62 cm.) and slightly backward so as to ensure contact

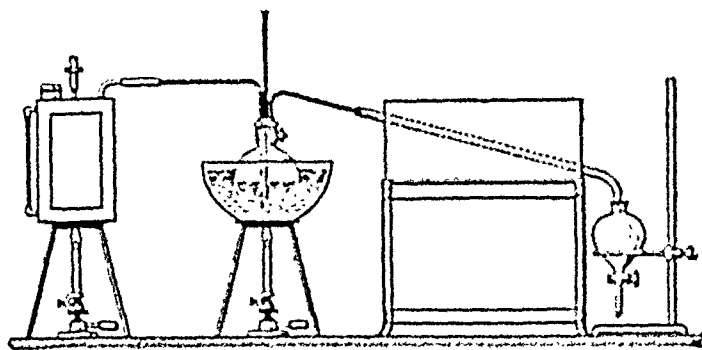


FIG. 28-32. Assembly of Distillation Apparatus. (Courtesy ASTM.)

with the wall of the graduate at a point 1 to  $1\frac{1}{4}$  in. (2.54 to 3.18 cm.) below the top of the graduate when it is in position to receive the distillate.

A separatory funnel having a capacity of not less than 500 ml. should be provided. Accessories consist of suitable ring stands for supporting the steam generator, distilling flask, bath for distilling flask, separatory funnel, and a thermometer.

The apparatus shall be assembled as shown in Fig. 28-32. The steam generator shall be filled with water and heat applied. The bath shall be filled with a high-flash-point oil and raised to approximately 140°C. (284°F.). Five hundred milliliters of the sample shall be weighed into the round-bottom flask. The connection shall be made from the steam generator to the steam delivery tube, the end of which shall be within  $\frac{1}{2}$  in. of the bottom of the distilling flask. The outlet from the distilling flask shall be connected to the condenser and the separatory funnel placed in position at the outlet of the condenser to receive the distillate. The end of the bulb of the thermometer in the steam-distilling flask shall be placed within  $\frac{1}{2}$  in. (12.7 mm.) of the bottom of the distilling flask.

When the temperature of the sample in the distilling flask reaches 130°C. the outlet of the steam generator shall be closed, thus forcing the steam to pass through the sample. The flow of steam shall be adjusted so that the distillate is collected at the rate of approximately 6 to 10 ml. per minute. The distillation shall be stopped when 100 ml. of the distillate contains not more than 0.5 ml. of solvent, as determined by measuring the amount of oil in 100 ml. of distillate. When the distillation is finished, the water shall be separated from the distillate and the distillate measured and retained for further tests, if required by the specifications.

In some cases, the distillate does not separate readily from the water, and this separation can be facilitated by the addition of sodium chloride, which will result

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in a sufficient difference in gravity to produce a clear separation of the two layers.

The results shall be reported in per cent by weight or volume as required by the specifications, based on the weight of the sample taken.

### RECOVERY AND EXAMINATION OF PIGMENT AND FILLER

Dilute 100 g. of the well-mixed material with 500 ml. of benzene in an 800-ml. stoppered flask. Either centrifuge or let stand in a warm place until the pigment or filler has settled, then carefully decant the supernatant liquid into a clean flask of large capacity. The pigment or filler is shaken up with 250 ml. more benzene, allowed to stand in a warm place until it settles, and the supernatant liquid decanted into the second flask. Repeat the treatment with benzene until the vehicle has been completely extracted from the pigment. The prevention of skin formation during this process may be attained by the addition of anti-oxidants such as phenol or hydrochinone (dissolved in ether), which are subsequently expelled on heating the pigment and base. The combined extracts are allowed to stand quietly to recover any pigment that may have been carried over with the benzene, and then carefully decanted through a weighed Gooch crucible provided with an asbestos filter. The residues in the flask and on the Gooch crucible are washed with benzene as before, and combined with the balance of pigment or filler, which is then dried at 110°C. and weighed. The combined extracts are retained for further examination.

The pigments or filler recovered from the previous test are subjected to a qualitative or quantitative analysis for purposes of identification, and to granulometric tests.

### RECOVERY AND EXAMINATION OF THE BASE

If no pigments or fillers are present, the base is recovered as described, and its percentage by weight ascertained directly. If pigments or fillers are present, the combined extracts are distilled to a small bulk, transferred to a tared dish, and evaporated in an oven at 110°C. *exactly* to the calculated weight of the base, by subtracting the weights of solvent and pigment or filler from the original weight of material taken for examination. When oxidizable substances are present, the final evaporation should take place in an atmosphere of nitrogen gas.

The base will contain the bituminous constituents (with the exception of any "free carbon" associated with coal-tar pitch, or the like, which will be separated with the pigments and fillers), and animal and vegetable oils or fats, resins, and metallic bases and driers. It may be separated into its component parts as follows:

## METHOD OF ANALYZING THE SEPARATED BASE

Dissolve 50 g. in 150 ml. benzene. Add 10 ml. dilute nitric acid (1:1) and boil under a reflux condenser for one-half hour to decompose any metallic soaps (i.e., driers, etc.). Add 150 ml. water, boil under reflux condenser, transfer to a separatory funnel, draw off the aqueous layer, boil with another 100 ml. water, and repeat if necessary until all the metals are removed.

### Benzene Solution:

Distill to 100 ml., add 300 ml. of the saponifying liquid,\* boil under reflux condenser for 1 hour, and separate the unsaponifiable and saponifiable constituents as described.

### Aqueous Extract:

Contains the metallic bases as nitrates. Examine qualitatively and then quantitatively for lead, manganese, cobalt, zinc, calcium, and magnesium.

### Unsaponifiable Matter:

Examine a small portion. If higher alcohols are present, separate the balance into:

### Saponifiable Matter:

Separate the fatty and resin acids as described.

### Aqueous Layer:

Determine percentage glycerol. Multiply this by 10 to estimate per cent of vegetable or animal oils or fats (triglycerides) present in the original substance.

### Hydrocarbons:

Contain the bituminous substances (i.e., asphalt, coal-tar pitch, unsap. matter derived from fatty-acid pitch, etc.)

### Higher Alcohols, Etc.:

Contain cholesterol, etc., derived from wool grease, also the unsaponifiable constituents originally present in resins (4 to 8%).

### Fatty Acids:

Include acids derived from vegetable and animal oils or fats, also from fatty-acid pitch.

### Resin Acids:

Include acids derived from rosin and the fossil resins.

(N.B.—The last three used for hardening rosin. The metallic driers should not be found by ignition, since the lead will be reduced to metal by the organic matter, and volatilized.)

\* The saponifying liquid shall consist of a 10% solution of KOH dissolved in equal parts of 95%  $C_2H_5OH$  or 90% benzene.

# PART V

## EXAMINATION OF BITUMINOUS DISPERSIONS

The examination of bituminous emulsions has been standardized by the ASTM as "Standard Methods of Testing Emulsified Asphalts" under the designation D244-60 and D244-61T as follows:

### WATER CONTENT

**Apparatus.**—The apparatus shall consist of a metal still or glass flask, heated by suitable means and provided with a reflux condenser discharging into a trap connected to the still or flask. The trap serves to collect and measure the condensed water and to return the solvent to the still. The type of distilling apparatus used is not an essential feature of this method.

**Metal Still.**—The metal still, Fig. 28-33(a), shall be a vertical cylindrical vessel, preferably of copper, having a faced flange at the top to which the head is tightly attached by means of a clamp. The head shall be of metal, preferably of brass or copper, and shall be provided with a tubulation 1 in. in inside diameter.

**Glass Still.**—The glass flask, Fig. 28-33(b), shall be of the short-neck, round-bottom type, made of well-annealed glass, having an approximate capacity of 500 ml.

**Heat Source.**—The burner used with the metal still shall be a ring gas burner 100 mm. (4 in.) in inside diameter. With the glass flask, an ordinary gas burner or electric heater may be used as the source of heat.

**Condenser.**—The condenser shall be of the water-cooled, reflux, glass tube type, having a condenser jacket not less than 400 mm. (15¾ in.) in length, with an inner tube 9.5 to 12.7 mm. (¾ to ½ in.) in outside diameter. The end of condenser to be inserted in the trap shall be ground off at an angle of  $30^{\circ} \pm 5^{\circ}$  from the vertical axis of the condenser.

**Trap.**—The trap shall be made of well-annealed glass, constructed in accordance with Fig. 28-33(c), and shall be graduated from 0 to 2 ml. in 0.1-ml. divisions, and from 2 to 25 ml. in 0.2-ml. divisions. The tolerance of the graduations between 0 and 2 ml. shall be  $\pm 0.05$  ml. and between 2 and 25 ml. shall be  $\pm 0.1$  ml.

The solvent used when testing bituminous emulsions shall be a coal-tar naphtha or a light oil, and shall conform to the following distillation requirements, determined in accordance with the Standard Method of Test for Distillation of Gasoline, Naphtha, Kerosene, and Similar Petroleum Products (ASTM D86-61).

**NOTE.**—98% shall distill between 248°F. (120°C.) and 482°F. (250°C.).



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The sample shall be thoroughly representative of the material to be tested, and the portion of the sample used for the test shall be thoroughly representative of the sample itself. Deviation from this requirement shall not be permitted.

NOTE.—The difficulties in obtaining proper representative samples for this determination are unusually great, so that the importance of sampling cannot be too strongly emphasized.

Procedure.—(a) When the material to be tested contains less than 25% of water, place exactly 100 g. of sample in the still or flask. When the material contains

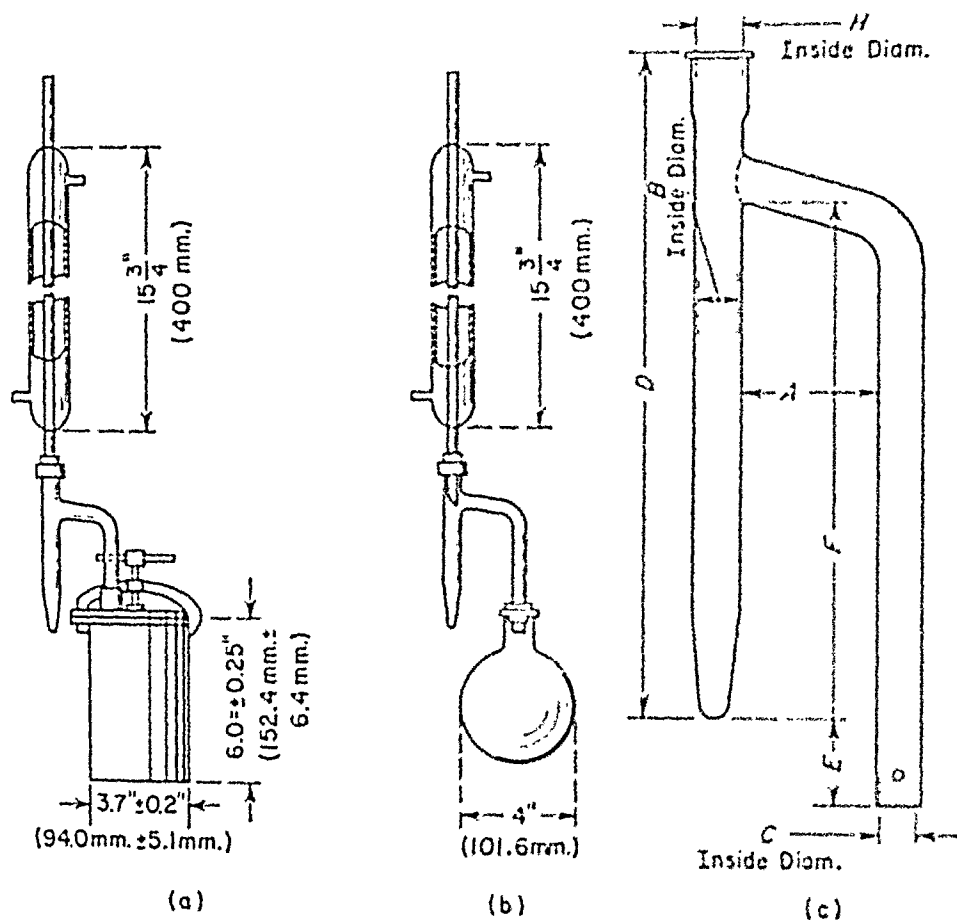


FIG. 28-33. Apparatus for Determining Water: A, 15 to 55 mm.; B, 11 to 16 mm.; C, 12 to 16 mm.; D, 235 to 255 mm.; E, 25 to 38 mm.; F, 186 to 191 mm.; H, 18 to 19 mm. (Courtesy ASTM.)

more than 25% of water, use a 50-g. sample. Thoroughly mix the sample to be tested with an equal volume of solvent by swirling, taking proper care to avoid loss of material.

(b) Make connections between the still or flask, trap, and condenser by means of tight-fitting corks as shown in Figs. 28-33(a) and 28-33(b). Adjust the end of the condenser inserted in the trap to that position which will allow the end to be submerged to a depth of not more than 1 mm. (0.04 in.) below the surface of the liquid in the trap after distillation conditions have been established. When the metal still is used, insert a heavy paper gasket moistened with the solvent between the lid and flange before attaching the clamp. Insert a loose cotton

plug in the top of the condenser tube to prevent condensation of atmospheric moisture.

(c) Then apply heat and so regulate it that the condensed distillate falls from the end of the condenser at the rate of from two to five drops per second. Place the ring burner used with the metal still about 3 in. above the bottom of the still at the beginning of the distillation, and gradually lower it as the distillation proceeds.

(d) Continue the distillation at the specified rate until no water is visible on any part of the apparatus except at the bottom of the trap. This operation usually requires less than 1 hour. Remove any persistent ring of condensed water in the condenser tube by increasing the rate of distillation for a few minutes.

Calculate the results as follows: The volume of condensed water measured in the trap at room temperature, multiplied by 100 and divided by the weight of sample used, is the percentage of water. Report as ". . . per cent water by weight, ASTM Method D244-61T."

Duplicate determinations of water by this method should not differ from each other by more than one division on the trap.

### RESIDUE BY DISTILLATION

**Procedure.**—(a) Place exactly 200 g. of a well-mixed and representative sample of the emulsion in the previously weighed iron still (including lid, clamp, thermometer, and gasket, if gasket is used) (Fig. 28-34).

(b) A gasket of oiled paper may be used between the still and its cover, or the joint may be ground to a tight fit. Clamp the cover securely on the still.

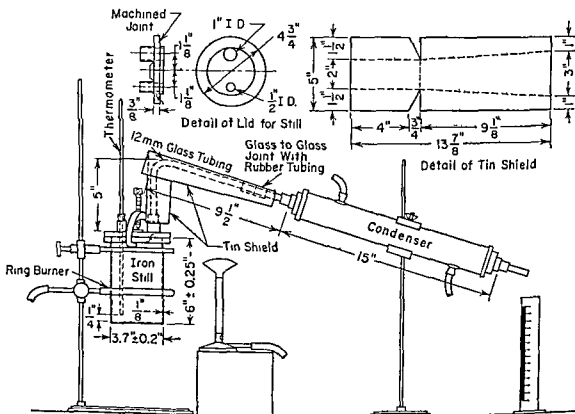


FIG. 28-34. Apparatus Assembly for Distillation Test of Emulsified Asphalts. (Courtesy ASTM.)



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resumption of heating, watch the delivery tube carefully and repeat this procedure if necessary.

When the residue has reached and remained at 500°F. (260°C.) for 15 minutes, proceed as described in paragraph (f) for the regular still. Although the distillation should be completed in not less than 1 hour nor more than 1½ hours from the first application of heat to the still, the maximum stated is not mandatory, as a longer time may be required in some cases to avoid foaming of the emulsion into the condenser.

If the residue in the still, prior to pouring the ductility and penetration samples, appears granular or heterogeneous in any way, stir with a spatula until the material runs from the spatula in strings instead of drops, and then pour.

### RESIDUE BY EVAPORATION

**Procedure A.**—(a) Procedure A shall be used when determination of residue only is required.

(b) Weigh exactly 50 g. of thoroughly mixed emulsified asphalt, representative of the sample, into each of three beakers, each beaker and a glass rod having previously been tared. Place the beakers containing the rods and sample in the oven, the temperature of which has been adjusted to  $325^{\circ} \pm 5^{\circ}\text{F.}$  ( $163^{\circ} \pm 2.8^{\circ}\text{C.}$ ), for 2 hours. At the end of this period remove each beaker and stir the residue thoroughly. Replace in the oven for 1 hour, then remove the beakers from the oven, allow to cool to atmospheric temperature, and weigh.

(c) Calculate the percentage residue on each beaker as follows:

$$\text{Residue, \%} = \frac{A - B}{C} \times 100$$

where  $A$  = weight of beaker, rod, and residue

$B$  = weight of tared beaker and rod

$C$  = weight of sample

Report the residue by evaporation as the average of the three results.

**Procedure B.**—(a) Procedure B shall be used when tests on residue from emulsion are required, in addition to percentage residue.

(b) Follow the procedure as described in Procedure A, paragraph (b), except to dehydrate four 50-g. samples. After the residue has been determined and calculated, replace the beakers in the oven until the asphalt residue is sufficiently fluid to pass through a No. 50 (297 micron) sieve (usually requiring 15 to 30 minutes). Then pour the residue through the No. 50 sieve and into suitable containers and molds for making such tests as desired, as described under Examination of Residue (p. 1052) (NOTE).

NOTE.—As the method for residue by evaporation described above tends to give an asphaltic residue lower in penetration and ductility than the distillation method, material may be accepted, but shall not be rejected as failing to meet specifications containing requirements for determination of residue by distillation, on data obtained by evaporation. If residue from evaporation fails to meet the requirements for properties specified for residue from distillation, tests shall be rerun, using the distillation method. (Usually, however, results by evaporation do fall within requirement limits set for residue by distillation.)

### CONSISTENCY TEST (VISCOSITY)

**Apparatus.**—The apparatus shall be the following:

(a) **Viscosimeter.**—A Saybolt Furol viscosimeter conforming to the requirements specified in the Standard Method of Test for Saybolt Viscosity (ASTM D88-56).

(b) *Sieve*.—A No. 20 (840 micron) sieve or a 20-mesh strainer of iron wire cloth, framed or unframed.

*Procedure*.—(a) Determine the viscosity at either 77°F. (25°C.) or 122°F. (50°C.) and express it in seconds, Saybolt Furol, which is the time in seconds, for the delivery of 60 ml. of emulsion.

(b) Although the Saybolt Furol viscosimeter is not used for petroleum products and lubricants when the time of flow is less than 25 seconds, this instrument is satisfactory for testing emulsified asphalt when the time of flow is not less than 20 seconds.

(c) Tests at 77°F. (25°C.). Stir the sample thoroughly without incorporating bubbles in it, and then pour it into a 4-ounce bottle. Place the bottle in the water bath at 77°F. (25°C.) for 30 minutes, and then mix the sample in the bottle by inverting it several times, slowly enough to prevent bubble formation. Pour the sample into the viscosity tube through the No. 20 (840 microns) sieve or 20-mesh strainer, allowing a small portion to flow through the outlet tube to waste. Place the cork in position, fill the tube and, without again stirring the sample, determine the viscosity as prescribed in ASTM Method D88-56.

(d) Tests at 122°F. (50°C.). Stir the sample thoroughly without incorporating bubbles in it, and then pour approximately 100 ml. into a 400-ml. glass beaker. Immerse the beaker containing the emulsion in a  $160^{\circ} \pm 5^{\circ}\text{F.}$  ( $71^{\circ} \pm 3^{\circ}\text{C.}$ ) water bath to a point where the bottom of the beaker will be approximately 2 in. below the surface of the water. Maintain the beaker in an upright position with the bottom parallel to the surface of the water. Stir the emulsion with a circular motion 60 times per minute, with the oil-tube thermometer in direct contact with the bottom and sides of the beaker, to obtain uniform temperature distribution. Take care to avoid incorporation of bubbles. Heat the emulsion under test in a 160°F. (71°C.) water bath to  $124.5^{\circ} \pm 0.5^{\circ}\text{F.}$  ( $51.1^{\circ} \pm 0.3^{\circ}\text{C.}$ ). With the cork stopper in the lower end of the air chamber at the bottom of the oil tube, immediately pour the emulsion through the 20-mesh strainer into the previously cleaned and dried oil tube until it ceases to overflow into the gallery. Stir the emulsion in the oil tube at 60 r.p.m. with the oil-tube thermometer until the test temperature is attained, taking care to prevent bubble formation. Adjust the bath temperature until the emulsion temperature in the tube remains constant for 1 minute at  $122^{\circ} \pm 0.1^{\circ}\text{F.}$  ( $50^{\circ} \pm 0.05^{\circ}\text{C.}$ ). Then withdraw the oil-tube thermometer and quickly remove the surplus emulsion from the gallery by means of the withdrawal tube so that the level of the emulsion in the gallery is below the level of the oil tube proper. Determine the viscosity as described in ASTM Method D88-56. Report the results to the nearest full second.

With proper attention to details, results in different laboratories should not differ by more than 5.0%.

### STABILITY TEST (DEMULSIBILITY)

*Apparatus and Reagents*.—The apparatus and reagents shall be as follows:

(a) *Wire Cloth*.—Three pieces of No. 14 (1410 micron) iron wire cloth approximately 5 in. square, unframed, having wire diameters and openings which conform to ASTM Specification E11.

(b) *Beakers*.—Three metal beakers of 600-ml. capacity each.

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(c) Rods.—Three metal rods with rounded ends, approximately  $\frac{5}{16}$  in. in diameter.

(d) Buret.—A 50-ml. glass buret graduated in 0.1-ml. intervals.

(e) Calcium chloride solution, 0.02 *N*.

(f) Calcium chloride solution, 0.10 *N*.

*Procedure.*—(a) Determine the percentage of residue by distillation as described under Procedure for Residue by Distillation.

(b) Record the weight of each assembly of beaker, rod, and wire cloth.

(c) Weigh exactly 100 g. of the emulsified asphalt into each of three 600-ml. tared beakers. Over a period of approximately 2 minutes, add to each beaker, from a buret, 35 ml. of 0.02 *N*  $\text{CaCl}_2$  solution if quick-setting emulsion is being tested, or 50 ml. of 0.10 *N*  $\text{CaCl}_2$  solution if mixing-type emulsion is being tested. While adding the solution of  $\text{CaCl}_2$ , stir the contents of the beaker continuously and vigorously, kneading lumps against the sides of the beaker to ensure thorough mixing of the reagent with the emulsion. Continue kneading the lump for another 2 minutes after the addition of the  $\text{CaCl}_2$  solution. Perform this operation after bringing the weighed sample of emulsion and the reagent to the standard temperature of  $77^\circ \pm 1.0^\circ\text{F}$ . ( $25^\circ \pm 0.5^\circ\text{C}$ ).

(d) Fit one of the wire cloths over a beaker or other suitable vessel and pour the mixture of emulsion and reagent through the wire cloth. Rinse the beaker containing the sample and metal rod with distilled water. Knead and break up all lumps, and continue washing the beaker, rod, and wire cloth until there is no longer any appreciable color imparted to the wash water. After washing as directed, place the beaker, rod, and wire cloth used in each individual test in a drying oven, and dry to constant weight at  $325^\circ\text{F}$ . ( $163^\circ\text{C}$ ).

The total weight thus obtained, less the total tare weight of the beaker, rod, and wire cloth, is the weight of the residue by the demulsibility test. Calculate the percentage demulsibility of the sample tested as follows:

$$\text{Demulsibility, \%} = \frac{A}{B} \times 100$$

where *A* = average weight of residue in grams from three tests of each individual sample of emulsified asphalt

*B* = weight of residue in grams per 100 g. of emulsion obtained in the test for residue by distillation described under Procedure for Residue by Distillation.

### SETTLEMENT TEST

*Apparatus.*—The apparatus shall be as follows:

(a) Cylinders.—Two 500-ml. glass cylinders, with pressed or molded glass bases and cork or glass stoppers. The outside diameter shall be  $5.0 \pm 0.5$  cm., and the cylinders shall be graduated at each 5-ml. interval to the 500-ml. mark.

(b) Glass Pipet.—A 60-ml. siphon, glass-tube pipet of optional form.

*Procedure.*—(a) Place a 500-ml. sample, representative of the emulsion, in each of the two glass cylinders. Stopper the cylinders in an airtight manner and allow them to stand unmolested, at laboratory air temperature, for 5 days. After standing for this 5-day period, remove approximately the first 55 ml. of emulsion by means of the pipet or siphon from the top of each cylinder without disturbing the balance of its contents. Weigh exactly 50 g. of each of the two samples, after each has been thoroughly mixed separately, into separate 600-ml. low-form glass

## EXAMINATION OF BITUMINOUS DISPERSIONS 1049

beakers, and determine the asphaltic residue by evaporation at 325°F. (163°C.) for 3 hours in the apparatus described in ASTM Method D6-39T.

(b) After removal of the first sample, siphon off approximately the next 390 ml. from each of the cylinders. Mix the residue remaining in the cylinders thoroughly and exactly, weigh out 50 g. from each of them, and determine for the two samples the amount of asphaltic residue (all sediment, if any, included) by evaporation as described in paragraph (a).

(c) Record the numerical difference between the average percentage of asphaltic residue found in the two top samples and that found in the two bottom samples.

### CEMENT MIXING

The high-early-strength Portland cement used in the test shall conform to the requirements for type III of the Standard Specifications for Portland Cement (ASTM C150-61), and shall have a minimum specific surface area of 1900 sq. cm. per g.

*Procedure.*—(a) Dilute the emulsion to be tested with distilled water to a residue of 55% as determined by either distillation, or evaporation for 3 hours at 325°F. (163°C.).

(b) Sieve a portion of the cement through the No. 80 (177 micron) sieve. Weigh 50 g. of the cement passing the No. 80 sieve into the iron dish.

(c) Add 100 ml. of the diluted emulsion to the cement in the dish, and stir the mixture at once with the steel rod, using a circular motion, making 60 complete revolutions during 1 minute. Immediately at the end of the 1-minute mixing period, add 150 ml. of distilled water, and continue the stirring for 3 minutes. Maintain the ingredients and apparatus at a temperature of approximately 77°F. (25°C.) during the mixing period.

(d) Pour the mixture through the tared No. 14 (1410 micron) sieve, of approximately 3-in. diameter, and rinse by pouring distilled water from a receptacle held at a height of approximately 6 in. Place the sieve in a tared shallow pan, heat at 325°F. (163°C.) in an oven until dry, and weigh.

Report the weight in grams of the material retained on the sieve and in the pan as the percentage of the emulsion broken.

### SIEVE TEST

*Apparatus and Reagents.*—The apparatus and reagents shall be as follows:

(a) *Sieve.*—A sieve having a 3-in. frame conforming to Sections 4(a) and (b) of ASTM Specifications E11-61, and having No. 20 (840 micron) wire sieve cloth conforming to Section 14(b) of these specifications.

(b) *Pan.*—A tin box cover or shallow metal pan of appropriate size to fit over the bottom of the standard sieve.

(c) *Sodium oleate solution* (2%), of pure sodium oleate in distilled water.

*Procedure.*—Record the weight of the sieve and pan, and then wet the wire cloth of the No. 20 sieve with the 2% sodium oleate solution. Weigh and pour exactly 1000 g. of the emulsified asphalt through the wire sieve, thoroughly washing the container and the residue on the sieve with the sodium oleate solution until the washings run clear. Place the pan under the sieve and heat for 2 hours in a drying oven whose interior temperature is held at 220°F. (105°C.), then cool in a desiccator, and weigh.

The total weight of the sieve, pan, and residue in grams less the combined tare

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weight of the sieve and pan, is the weight of the residue by the sieve test. Calculate the percentage of residue retained on the sieve from this weight.

### COATING TEST

This test is applicable only to emulsions containing a base of asphalt of semi-solid consistency employed for coating aggregates. It is not applicable to the so-called quick-setting type of emulsions.

*Apparatus.*—The apparatus and material shall be as follows:

(a) *Screens.*—Standard  $\frac{3}{4}$ -in. and  $\frac{1}{4}$ -in. round-hole screens conforming to ASTM Specifications E11-61.

(b) *Spatula.*—A steel spatula or its equivalent, having a blade approximately 8 in. in length.

(c) *Dish.*—A round-bottom, iron dish or a kitchen saucepan, of approximately 1-quart capacity.

(d) *Stone.*—A supply of reference stone (hard limestone, trap rock, or other type) which has been washed with water and dried before using. The grading of this stone shall be such that it will all pass through a standard  $\frac{3}{4}$ -in. screen and not more than 5% will pass through a  $\frac{1}{4}$ -in. screen.

*NOTE.*—Each laboratory shall select its own reference stone supply, the source of which is not apt to change. This is to obviate rapid changes in the character of reference stone used in any one laboratory.

*Procedure.*—(a) Weigh exactly 465 g. of the washed and dried graded stone, and place it in the metal pan.

(b) Add a 35-g. sample of the emulsion to the stone in the pan, and mix vigorously with the spatula for 3 minutes.

(c) Record whether or not there is appreciable separation of the asphaltic base from the water of the emulsion, and whether or not the stone is uniformly and thoroughly coated with the emulsion.

### MISCIBILITY WITH WATER

Test A is applicable to the so-called quick-setting type of emulsions.

*Procedure.*—To about 50 ml. of the emulsion, gradually add about 150 ml. of distilled water, stirring the mixture while adding the water. The temperature is not important, but should be between 70° and 77°F. (21° and 25°C.). Allow the mixture to stand for 2 hours and then examine it for any appreciable coagulation of the asphalt content of the emulsion.

Test B is used for determining the miscibility with water of medium-setting and slow-setting types of asphalt emulsions. It is not applicable to the quick-setting type of asphalt emulsions.

*Apparatus.*—The apparatus shall be as follows:

(a) *Glass Tubes.*—Three glass tubes, 7 mm. in outside diameter, 5 mm. in inside diameter, and 15 cm. in length, fitted with suitably bored No. 8 corks, adjusted as described subsequently under Assembly of Apparatus.

(b) *Supporting Strip.*—A strip of metal or wood, approximately 15 cm. in length, 2.5 cm. in width, and 0.5 cm. in thickness, with a hole 10 mm. in diameter in the center.

(c) *Crucibles.*—Three 15- or 25-ml. porcelain crucibles, or three 30-ml. beakers of heat-resistant glass.



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*Assembly of Apparatus.*—Adjust the position of the corks on the glass tubes by measuring 200 ml. of distilled water at 68° to 77°F. (20° to 25°C.) into the 400-ml. beaker, placing the supporting strip across the top of the beaker, inserting a tube through the hole, and adjusting the position of the cork so that when the tube is supported by the cork resting on the supporting strip, the lower end of the tube is immersed in the water to a depth of 1 cm. below the surface. In the same manner, adjust the second and third tubes so that the depth of immersion is 2.5 and 4.6 cm., respectively.

NOTE.—Due to slight differences in height and diameter of 400-ml. beakers as obtained commercially, it may be necessary to readjust the tubes when used in different beakers. In any event, the third or bottom tube shall project into the emulsion so that the tip is within 1 to 1.5 mm. of the bottom of the beaker.

*Procedure.*—(a) Measure 50 ml. of the emulsion at a temperature of 68° to 77°F. (20° to 25°C.) into a 50-ml. graduated cylinder and transfer to the 400-ml. beaker. Wash the graduate with three 50-ml. portions of distilled water at 68° to 77°F. (20° to 25°C.) and add the washings to the beaker, bringing the final volume to 200 ml. Stir the emulsion and water with a glass rod until uniformly mixed, cover the beaker with a watch glass, and allow the mixture to stand undisturbed for 2 hours.

(b) Weigh the three crucibles or 30-ml. beakers, and a watch glass for each, to the nearest 0.1 mg. After the diluted emulsion has stood for 2 hours, remove the watch glass and place the supporting strip across the top of the 400-ml. beaker. Take a sample of approximately 1 g. from the top layer and transfer to one of the crucibles or beakers, using the first or 1-cm. depth tube as a pipet. Close the top of the tube with the finger, insert the tube to the proper depth, remove the finger while the emulsion rises in the tube, and then replace the finger on top of the tube so that when the tube is removed its contents of emulsion will be pipetted from the beaker. After removal, wipe off the adhering liquid on the outside of the tube with filter paper before transferring the sample to the crucible. In like manner, take samples from the middle and bottom of the diluted emulsion, using the second and third tubes, respectively. Weigh the crucibles with their accompanying samples of emulsion, and determine the weight of each of the three samples by difference. Cover the crucibles with watch glasses to retard evaporation.

(c) Remove the watch glasses from the crucibles and place the samples in an oven at 163°C. (325°F.) for 2 hours; then remove, cool, and weigh.

Calculate the percentage of asphalt residue in the top, middle, and bottom levels. Report the maximum numerical difference in percentage of asphalt content between any two of the three levels.

### FREEZING TEST

*Procedure.*—(a) Place approximately 400 g. of the emulsion in a clean metal container, such as a 1-pint press-top tin.

(b) Expose the emulsion in the closed container to a temperature of 0°F. (−17.8°C.) for 12 or more consecutive hours.

(c) At the expiration of the freezing period, permit the emulsion to thaw by exposure of the container to the temperature of the laboratory.

(d) After the first operation of freezing and thawing, repeat the procedure twice, so that the emulsion will have been subjected to three cycles of freezing and thawing.

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(c) After the third cycle, the emulsion may be homogeneous or may have separated into distinct layers which cannot be rendered homogeneous by stirring at laboratory temperature.

(f) Report the result of this test as either "Homogeneous" or "Broken."

### EXAMINATION OF RESIDUE

#### SPECIFIC GRAVITY

*Procedure.*—Determine the specific gravity on a representative portion of the residue in accordance with the Standard Method of Test for Specific Gravity of Road Oils, Road Tars, Asphalt Cements, and Soft Tar Pitches (ASTM D70).

#### ASH CONTENT

*Procedure.*—Determine the ash on a representative portion of the residue in accordance with the rapid routine method of ash determination, as described in Section 5 of the Standard Methods of Analysis of Lubricating Grease (ASTM D128)

#### SOLUBILITY IN CARBON DISULFIDE

*Procedure.*—Determine the solubility in carbon disulfide on a representative portion of the residue in accordance with the Standard Method of Test for Bitumen (ASTM D4).

#### PENETRATION

*Procedure.*—Determine the penetration on a representative portion of the residue in accordance with the Standard Method of Test for Penetration of Bituminous Materials (ASTM D5).

#### DUCTILITY

*Procedure.*—Determine the ductility on a representative portion of the residue in accordance with the Standard Method of Test for Ductility of Bituminous Materials (ASTM D113).

NOTE—Other tests having reference to bituminous dispersions are as follows:

- 1 ASTM D1167-58T—"Asphalt-Base Emulsions for Use as Protective Coatings for Built-Up Roofs"
2. ASTM D1010-58—"Asphalt Emulsions for Use as Protective Coatings for Metal"
- 3 ASTM D466-42—"Films Deposited from Bituminous Emulsions"

## Chapter 29

# PORTLAND CEMENT

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**Introduction.**—Portland cement is the product obtained by pulverizing clinker consisting essentially of hydraulic calcium silicates.

The methods of chemical analysis included in this chapter are principally applicable to the five types of portland cement specified by the American Society for Testing and Materials, the U. S. Government, and the American Association of State Highway Officials, with added methods of chemical analysis for raw materials used in the manufacture of these cements. The methods of chemical analysis as applied to portland cement will be principally current ASTM procedures. ASTM and Federal methods of chemical analysis of portland cement differ only in minor detail. For details of Federal methods refer to current Federal Test Method Standard No. 158.

## SAMPLING

A section on sampling of portland cement is included in order to point out the importance of sampling in relation to chemical determinations.

In mining operations it is common to sample on an "assay basis" because the information desired demands that samples representative of the whole be obtained; however, when a product must meet certain maximum and minimum requirements, the purpose and possibly the method of sampling may be considered from a different point of view.

There are at least two schools of thought as applied to the sampling of Portland cement. One favors the "grab method," whereas a second subscribes to the "composite method." Those favoring the "grab method" are of the opinion that samples taken at irregular intervals during production and tested separately will more accurately detect variations that fall outside specification requirements. Those favoring the "composite method" feel that samples taken at regular intervals during production and combined in approximately equal weights will more nearly be representative of the storage bin filled and the individual shipments from the bin.

Since a difference of opinion exists, the method used is usually determined by the purchaser. For details of accepted sampling procedures refer to current American Society for Testing and Materials Specifications under designation C183 and current Federal Test Method Standard No. 158. Also see chapter on sampling, p. 21.

## STANDARD METHODS OF CHEMICAL ANALYSIS OF PORTLAND CEMENT

Methods applicable to chemical analysis of portland cement have been standardized by the ASTM under the designation C114-58.<sup>1</sup>

These methods of chemical analysis are not all considered as possessing the highest obtainable accuracy, but are methods to be followed in making acceptance tests on cements covered by specifications requiring that tests be made in accordance with the analytical procedures contained in this standard.

### REFEREE METHODS

Referee analyses, when there is a question regarding acceptance, shall be made in duplicate and the analyses shall be made on different days. If the two results do not agree within the permissible variation given in Table 29-1, the determination

TABLE 29-1. MAXIMUM PERMISSIBLE VARIATIONS IN RESULTS

Component	Between Two Results	Between the Extreme Values in Three Results
Silicon dioxide, $\text{SiO}_2$ .....	0.16	0.24
Aluminum oxide, $\text{Al}_2\text{O}_3$ .....	0.20	0.30
Ferric oxide, $\text{Fe}_2\text{O}_3$ .....	0.10	0.15
Calcium oxide, $\text{CaO}$ .....	0.20	0.30
Magnesium oxide, $\text{MgO}$ .....	0.16	0.24
Sulfur trioxide, $\text{SO}_3$ .....	0.10	0.15
Loss on ignition .....	0.10	0.15
Sodium oxide, $\text{Na}_2\text{O}$ .....	0.03	0.05
Potassium oxide, $\text{K}_2\text{O}$ .....	0.03	0.05
Water-soluble alkali .....	0.05	0.08
Phosphorus pentoxide, $\text{P}_2\text{O}_5$ .....	0.03	0.05
Manganic oxide, $\text{Mn}_2\text{O}_3$ .....	0.03	0.05
Insoluble residue.....	0.10	0.15
Chloroform-soluble organic substances.....	0.004	0.006
Free calcium oxide .....	0.20	0.30

shall be repeated until two or three results agree within the permissible variation. When two or three results do agree within the permissible variation, their average shall be accepted as the correct value. When either an average of two results or an average of three results can be calculated, the calculation shall be based on the three results. For the purpose of comparing analyses and calculating the average of acceptable results, the percentages shall be calculated to the nearest 0.01 (or 0.001 in the case of chloroform-soluble organic substances), although some of the average values are reported to 0.1 as indicated in the methods. When a blank determi-

<sup>1</sup> Reproduced in part with permission of the American Society for Testing and Materials.

nation is specified, one shall be made with each individual analysis or with each group of two or more samples analyzed on the same day for a given component.

NOTE.—It is recommended that the analyst use reference samples such as National Bureau of Standards Standard Sample No. 177 (portland cement) to indicate abnormal variations, if present.

### DETERMINATION OF SILICON DIOXIDE

*Procedure.*—(a) Transfer 0.5 g. of the sample to an evaporating dish, preferably of platinum for the sake of faster evaporation, moisten with 10 ml. of cold water to prevent lumping, add 5 to 10 ml. of HCl, and digest with the aid of gentle heat and agitation until solution is complete. Solution may be aided by light pressure with the flattened end of a glass rod. Evaporate the solution to dryness on a steam bath. Without heating the residue any further, treat it with 5 to 10 ml. of HCl and then an equal amount of water, or pour at once upon the residue 10 to 20 ml. of HCl (1:1). Then cover the dish and digest for 10 minutes on the bath or a hot plate. Dilute the solution with an equal volume of hot water, immediately filter, and wash the separated  $\text{SiO}_2$  thoroughly with hot water (NOTE 1), and reserve the residue.

NOTE 1.—The washing of the  $\text{SiO}_2$  precipitates can be made more effective by using hot HCl (1:99) and then completing the washing with hot water.

(b) Again evaporate the filtrate to dryness, and bake the residue in an oven for 1 hour at  $105^\circ$  to  $110^\circ\text{C}$ . Cool, and add 10 to 15 ml. of HCl (1:1) and heat on the bath or hot plate. Dilute with an equal volume of water, filter immediately on a fresh filter paper, and wash the small  $\text{SiO}_2$  residue thoroughly with hot water. Reserve the filtrate and washings for the determination of the ammonium hydroxide group (p. 1056).

(c) Transfer the papers containing the residues [paragraphs (a) and (b)] to a platinum crucible (NOTE 2). Dry and ignite the papers, first at a low heat until the carbon of the filter paper is completely consumed without flaming, and finally at  $1100^\circ$  to  $1200^\circ\text{C}$ . until the weight remains constant.

NOTE 2.—The empty crucible may be weighed if one wishes to know, for his own information, the magnitude of impurities in the residue of  $\text{SiO}_2$ .

(d) Treat the  $\text{SiO}_2$  thus obtained, which will contain small amounts of impurities, in the crucible with 0.5 to 1 ml. of water, two drops of  $\text{H}_2\text{SO}_4$  (1:1), and about 10 ml. of HF, and evaporate cautiously to dryness. Finally, heat the small residue at  $1050^\circ$  to  $1100^\circ\text{C}$ . for a minute or two, cool, and weigh. The difference between this weight and the weight previously obtained represents the amount of  $\text{SiO}_2$ . To this amount of  $\text{SiO}_2$ , add the amount of  $\text{SiO}_2$  recovered from the residue of the ammonium hydroxide group as directed in the analysis of the ammonium hydroxide group, paragraphs (d) and (e), given subsequently. Add 0.5 g. of  $\text{Na}_2\text{S}_2\text{O}_7$  or  $\text{K}_2\text{S}_2\text{O}_7$  to the crucible and heat below red heat until the small residue of impurities is dissolved in the melt. Cool, dissolve the fused mass in water, and add it to the filtrate and washings reserved for the determination of the ammonium hydroxide group.

Blank.—Make a blank determination, following the same procedure and using the same amounts of reagents, and correct the results obtained in the analysis accordingly.

**Calculation.**—Calculate the percentage of  $\text{SiO}_2$  to the nearest 0.10 by multiplying the weight in grams of  $\text{SiO}_2$  by 200 [100 divided by the weight of sample used (0.5 g.)].

### DETERMINATION OF THE AMMONIUM HYDROXIDE GROUP

**Procedure.**—(a) To the filtrate reserved in accordance with paragraph (b) of the procedure for silicon dioxide (p. 1055) (NOTE 1), which should have a volume of about 200 ml., add HCl if necessary to ensure a total of 10 to 15 ml. of the acid. Add a few drops methyl red indicator (2 g. per liter of ethanol), and heat to boiling. Then treat with  $\text{NH}_4\text{OH}$  (1:1) (NOTE 2), drop by drop, until the color of the solution becomes distinctly yellow and add one drop in excess (NOTE 3). Heat the solution containing the precipitate to boiling and boil for 50 to 60 seconds. In the event difficulty from bumping is experienced while boiling the ammoniacal solution, a digestion period of 10 minutes on a steam bath, or on a hot plate having the approximate temperature of a steam bath, may be substituted for the 50- to 60-second boiling period. Allow the precipitate to settle (in not more than 5 minutes) and filter. Wash, from two times for a small precipitate to four times for a large one, with hot  $\text{NH}_4\text{Cl}$  (20 g. per liter) (NOTE 4).

NOTE 1.—If a platinum evaporating dish has been used for the dehydration of  $\text{SiO}_2$ , iron may have been partially reduced. At this stage, add about 3 ml. of saturated bromine water to the filtrate and boil the filtrate to eliminate the excess bromine before adding the methyl red indicator.

NOTE 2.—The  $\text{NH}_4\text{OH}$  used to precipitate the hydroxides must be free of contamination with  $\text{CO}_2$ .

NOTE 3.—It usually takes one drop of  $\text{NH}_4\text{OH}$  (1:1) to change the color of the solution from red to orange and another drop to change the color from orange to yellow. If desired, the addition of the indicator may be delayed until  $\text{Fe}(\text{OH})_3$  is precipitated without  $\text{Al}(\text{OH})_3$  being completely precipitated. In such a case, the color changes may be better observed. However, if the content of  $\text{Fe}_2\text{O}_3$  is unusually great, it may be necessary to let the precipitate settle a little, a few times, before the proper end point is attained. If the color fades during the precipitation, add more of the indicator. Observation of the color where a drop of the indicator strikes the solution may be an aid in the control of the acidity. The boiling should not be prolonged as the color may reverse and the precipitate may be difficult to retain on the filter. The solution should be distinctly yellow when it is ready to filter. If it is not, restore the yellow color with more  $\text{NH}_4\text{OH}$  (1:1) or repeat the precipitation.

NOTE 4.—Two drops of methyl red indicator should be added to the  $\text{NH}_4\text{Cl}$  solution in the wash bottle, followed by  $\text{NH}_4\text{OH}$  (1:1) added dropwise until the color just changes to yellow. If the color reverts to red at any time due to heating, it should be brought back to yellow by the addition of a drop of  $\text{NH}_4\text{OH}$  (1:1).

(b) Set aside the filtrate and transfer the precipitate and filter paper to the same beaker in which the first precipitation was effected. Dissolve the precipitate in hot HCl (1:3), dilute the solution to about 100 ml., and reprecipitate the hydroxides as described in paragraph (a). Filter the solution, and wash the precipitate with two 10-ml. portions of hot  $\text{NH}_4\text{Cl}$  (20 g. per l.) (NOTE 4). Combine the filtrate and washings with the filtrate set aside and reserve for the determination of CaO (p. 1058).

(c) Place the precipitate in a weighed platinum crucible, heat slowly until the papers are charred, and finally ignite to constant weight at  $1050^\circ$  to  $1100^\circ\text{C}$ . with care to prevent reduction, and weigh as the ammonium hydroxide group.

(d) Add 3 g. of  $\text{Na}_2\text{S}_2\text{O}_7$  or  $\text{K}_2\text{S}_2\text{O}_7$  to the crucible (NOTE 5) and heat below red

heat until the residue is dissolved in the melt (NOTE 6). Cool, dissolve the fused mass in water containing 2.5 ml. of  $\text{H}_2\text{SO}_4$ , and evaporate the solution. Raise the temperature until copious fumes are evolved, but avoid a large loss of  $\text{H}_2\text{SO}_4$  which will cause the mass to become hard instead of pasty on cooling. Dissolve the mass in water, digest for 15 to 30 minutes short of boiling, filter, and wash with hot water.

NOTE 5.—The procedure described in paragraphs (d) and (e) is required only when a chemical determination fails to meet a specification requirement.

NOTE 6.—Start the heating with caution because pyrosulfates (also known as fused bisulfates), as received, often foam and spatter in the beginning, due to an excess of  $\text{H}_2\text{SO}_4$ . Avoid an unnecessarily high temperature and unnecessarily prolonged heating, as fused pyrosulfates may attack platinum. A supply of nonspattering pyrosulfate may be prepared by heating some pyrosulfate in a platinum vessel below red heat until the foaming and spattering cease, cooling, and crushing the fused mass.

(e) Transfer the paper (NOTE 5) containing the residue to a platinum crucible. Dry and ignite the paper, first at a low heat until the carbon of the paper is completely consumed without inflaming, and finally at  $1100^\circ$  to  $1200^\circ\text{C}.$  until the weight remains constant. Treat the  $\text{SiO}_2$  thus obtained in the crucible with a drop of water, about 5 ml. of  $\text{HF}$ , and a drop of  $\text{H}_2\text{SO}_4$ , and evaporate cautiously to dryness. Finally, heat the crucible at  $1050^\circ$  to  $1100^\circ\text{C}.$  for 1 to 2 minutes, cool, and weigh. The difference between this weight and the weight previously obtained represents the amount of residual  $\text{SiO}_2$ . Subtract this amount from the amount of ammonium hydroxide group obtained according to paragraph (c) and add the same amount to the amount of  $\text{SiO}_2$  obtained according to paragraph (d) of the Silicon Dioxide Determination (p. 1055).

Blank.—Make a blank determination, following the same procedure and using the same amounts of reagents, and correct the results obtained in the analysis accordingly.

Calculation.—Calculate the percentage of ammonium hydroxide group to the nearest 0.01 by multiplying the weight in grams of ammonium hydroxide group by 200 [100 divided by the weight of sample used (0.5 g.)].

### DETERMINATION OF FERRIC OXIDE

**Reagents.** Stannous Chloride Solution.—Dissolve 5 g. of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 10 ml. of  $\text{HCl}$  and dilute to 100 ml. Add scraps of iron-free granulated tin and boil until the solution is clear. Keep the solution in a closed dropping bottle containing metallic tin.

Barium Diphenylamine Sulfonate Indicator.—Dissolve 0.3 g. of barium diphenylamine sulfonate in 100 ml. of water.

Standard Potassium Dichromate Solution (1 ml. = 0.004 g.  $\text{Fe}_2\text{O}_3$ ).—Dissolve 2.457 g. of  $\text{K}_2\text{Cr}_2\text{O}_7$  in water and dilute to 1 liter. Standardize against standard Sibley iron ore issued by the National Bureau of Standards (standard sample No. 27 or its replacements) in the same manner (NOTE) as directed for the determination of  $\text{Fe}_2\text{O}_3$  in cement, using a weight of iron ore that will yield a titration within 3 ml. of that required by the cement sample in question.

Calculate the  $\text{Fe}_2\text{O}_3$  equivalent of the solution in grams per milliliter by multiplying the weight in grams of iron in the amount of iron ore used by 1.430 (molecular ratio of  $\text{Fe}_2\text{O}_3$  to  $2\text{Fe}$ ) and dividing by the volume in milliliters of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution required.

**NOTE.**—The iron ore may require long digestion in hot HCl for complete dissolution. Stannous chloride may be used as an aid in the dissolution, as follows: Treat the sample with 15 ml. of HCl and digest at a temperature just below boiling for about 30 minutes. Add some of the  $\text{SnCl}_2$  solution, using less than the amount that is expected to reduce all the iron. Continue the digestion until the iron is dissolved out, as evidenced by the absence of dark residue. The  $\text{SnCl}_2$  may be added in small quantities during the digestion. If an excess is present at the end of the digestion, destroy it with bromine water. Dilute the solution to about 50 ml., heat the solution to boiling, and proceed as directed for the determination of  $\text{Fe}_2\text{O}_3$  in cement, beginning with decolorization with  $\text{SnCl}_2$ .

**Procedure.**—To 1 g. of the sample, add 40 ml. of cold water and, while the mixture is stirred vigorously, add 10 ml. of HCl. If necessary, heat the solution and grind the cement with the flattened end of a glass rod until it is evident that the cement is completely decomposed. Heat the solution to boiling and treat it with the  $\text{SnCl}_2$  solution, added drop by drop while stirring, until the solution is decolorized. Add one drop in excess and cool the solution to room temperature. Rinse the inside of the vessel with water, and add all at once 10 ml. of a cool, saturated  $\text{HgCl}_2$  solution. Stir the solution vigorously for 1 minute and add 10 ml. of  $\text{H}_3\text{PO}_4$  (1:1) and two drops of barium diphenylamine sulfonate indicator. Add sufficient water so that the volume after titration will be between 75 and 100 ml. Titrate with the standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution. The end point is taken as the point at which a drop causes an intense purple coloration that remains unchanged on further addition of the standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

**Calculation.**—Calculate the percentage of  $\text{Fe}_2\text{O}_3$  to the nearest 0.01 (to be reported to the nearest 0.1) as follows:

$$\text{Fe}_2\text{O}_3, \% = EV \times 100$$

where  $E$  =  $\text{Fe}_2\text{O}_3$  equivalent of the  $\text{K}_2\text{Cr}_2\text{O}_7$  solution in grams per milliliter

$V$  = milliliters of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution required by the 1-g. sample used

### DETERMINATION OF ALUMINUM OXIDE

**Procedure.**—Calculate the percentage of  $\text{Al}_2\text{O}_3$  by deducting the percentages of  $\text{Fe}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$  (NOTE), determined according to the above procedure and to ASTM C114-58, Sections 24 and 25, respectively, and expressed to the nearest 0.01, from the percentage of ammonium hydroxide group, determined as described on p. 1056 and expressed to the nearest 0.01. Report to the nearest 0.1.

**NOTE.**—The determination of  $\text{P}_2\text{O}_5$  and its deduction from the determination of ammonium hydroxide group are required only when a sample fails to meet a specification requirement. Any titanium that may be present will be precipitated with  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  in the procedure described above and is counted as  $\text{Al}_2\text{O}_3$ . Aluminum oxide should not be corrected for  $\text{TiO}_2$  unless such a correction is expressly specified or the determination of the component is required.

### DETERMINATION OF CALCIUM OXIDE

**Procedure.**—(a) Acidify the combined filtrates obtained in the precipitations of the ammonium hydroxide group (p. 1056) with HCl and evaporate them to a volume of about 100 ml. Add 40 ml. of saturated bromine water to the hot solution and immediately add  $\text{NH}_4\text{OH}$  until the solution is distinctly alkaline. Boil the solution for 5 minutes or more, making certain that the solution is at all times distinctly alkaline.

Allow the precipitate to settle, filter, and wash with hot water. Discard any manganese dioxide that may have been precipitated. Acidify the filtrate with



HCl and boil until all the bromine is expelled. Add 5 ml. of HCl, dilute to 200 ml., and add a few drops of methyl red indicator and 30 ml. of warm ammonium oxalate solution (50 g. per l.). Heat the solution to 70° to 80°C., and add  $\text{NH}_4\text{OH}$  (1:1) dropwise, while stirring, until the color changes from red to yellow. Allow the solution to stand without further heating for 1 hour (no longer), with occasional stirring during the first 30 minutes. Filter and wash moderately with cold ammonium oxalate solution (1 g. per l.). Reserve the filtrate and washings.

(b) Transfer the precipitate and filter paper to the beaker in which the precipitation was effected. Dissolve the oxalate in 50 ml. of hot HCl (1:4) and macerate the filter paper. Dilute to 200 ml. with water, add a few drops of methyl red indicator and 20 ml. of ammonium oxalate solution, heat the solution nearly to boiling, and precipitate calcium oxalate again by neutralizing the acid solution with  $\text{NH}_4\text{OH}$  as described in paragraph (a). Allow the solution to stand 1 to 2 hours (standing for 2 hours at this point does no harm), filter, and wash as before. Combine the filtrate with that already obtained and reserve for the determination of MgO (see below).

(c) Dry the precipitate in a weighed, covered platinum crucible. Char the paper without inflaming, burn the carbon at as low a temperature as possible, and, finally, heat with the crucible tightly covered in an electric furnace or over a blast lamp at a temperature of 1100° to 1200°C. Cool in a desiccator and weigh as CaO. Repeat the ignition to a constant weight.

Blank.—Make a blank determination, following the same procedure and using the same amounts of reagents, and correct the results obtained in the analysis accordingly.

Calculation.—Calculate the percentage of CaO to the nearest 0.1 by multiplying the weight in grams of CaO by 200 [100 divided by the weight of sample used (0.5 g.)].

## DETERMINATION OF MAGNESIUM OXIDE

**Reagents.** Ammonium Nitrate Wash Solution.—Dissolve 100 g. of  $\text{NH}_4\text{NO}_3$  in water, add 200 ml. of  $\text{NH}_4\text{OH}$ , and dilute to 1 liter.

**Procedure.**—(a) Acidify the filtrates reserved in the determination of CaO (see above) with HCl and concentrate to about 250 ml. Add to this solution about 10 ml. of  $(\text{NH}_4)_2\text{HPO}_4$  (250 g. per l.) and cool the solution by placing in a beaker of ice water. After cooling, add  $\text{NH}_4\text{OH}$  drop by drop, while stirring constantly, until the crystalline magnesium ammonium phosphate begins to form, and then in moderate excess (5 to 10% of the volume of the solution), the stirring being continued for several minutes. Set the solution aside for at least 8 hours in a cool atmosphere, and then filter.

(b) Unfold the filter paper and, using hot water, wash the precipitate into the beaker in which the precipitation was effected. Rinse the filter paper with hot HCl (1:4) and again with hot water; if necessary, add more hot HCl (1:4) to dissolve the precipitate. Dilute the solution to about 100 ml., add 1 ml. of  $(\text{NH}_4)_2\text{HPO}_4$  (250 g. per l.), and then add  $\text{NH}_4\text{OH}$  drop by drop, while stirring constantly, until the precipitate is again formed as described and the  $\text{NH}_4\text{OH}$  is in moderate excess. Cool, allow to stand for about 2 hours, filter, and wash with two 10-ml. portions of the  $\text{NH}_4\text{NO}_3$  wash solution. Place in a weighed platinum or porcelain crucible, slowly char the paper, and carefully burn off the resulting carbon. Ignite the precipitate at 1100° to 1200°C. (Note) to constant weight, taking care to avoid melting the pyrophosphate.

**NOTE.**—If the crucible is glazed, the temperature should not exceed 1125°C. as the glaze may partially fuse at about 1200°C.

**Blank.**—Make a blank determination, following the same procedure and using the same amounts of reagents, and correct the results obtained in the analysis accordingly.

**Calculation.**—Calculate the percentage of MgO to the nearest 0.1 as follows:

$$\text{MgO, \%} = W \times 72.4$$

where  $W$  = grams of  $\text{Mg}_2\text{P}_2\text{O}_7$

72.4 = molecular ratio of  $2\text{MgO}$  to  $\text{Mg}_2\text{P}_2\text{O}_7$  (0.362) divided by weight of sample used (0.5 g.) and multiplied by 100

### DETERMINATION OF SULFUR TRIOXIDE

**Procedure.**—To 1 g. of the sample, add 25 ml. of cold water and, while the mixture is stirred vigorously, add 5 ml. of HCl. If necessary, heat the solution and grind the material with the flattened end of a glass rod until it is evident that decomposition of the cement is complete (NOTE 1). Dilute the solution to 50 ml. and digest for 15 minutes at a temperature just below boiling. Filter, and wash the residue thoroughly with hot water. Dilute the solution to 250 ml. and heat to boiling. Add slowly, drop by drop from a pipet, 10 ml. of hot  $\text{BaCl}_2$  (100 g. per l.) and continue the boiling until the precipitate is well formed. Digest the solution for 12 to 24 hours at a temperature just below boiling (NOTE 2). Take care to keep the volume of solution between 225 and 260 ml. and add water for this purpose if necessary. Filter the precipitate, wash, place the paper and contents in a weighed platinum or porcelain crucible, and slowly char and consume the paper without flaming. Then ignite at 800° to 900°C., cool in a desiccator, and weigh the  $\text{BaSO}_4$ .

**NOTE 1.**—A brown residue due to compounds of manganese may be disregarded. See NOTE 2 (p. 1068) under Determination of Insoluble Residue.

**NOTE 2.**—If a rapid determination is desired, the time of digestion may be reduced to as little as 3 hours. The result may be slightly low. If the cement is rejected for failure to meet the specification requirement, the time of digestion shall be 12 to 24 hours.

**Blank.**—Make a blank determination, following the same procedure and using the same amounts of reagents, and correct the results obtained in the analysis accordingly.

**Calculation.**—Calculate the percentage of  $\text{SO}_3$  to the nearest 0.1 as follows:

$$\text{SO}_3, \% = W \times 34.3$$

where  $W$  = grams of  $\text{BaSO}_4$

34.3 = molecular ratio of  $\text{SO}_3$  to  $\text{BaSO}_4$  (0.343) multiplied by 100.

**Optional Procedure.**—The acid filtrate obtained in the determination of the insoluble residue (p. 1068) may be used for the determination of  $\text{SO}_3$  instead of using a separate sample.

### DETERMINATION OF SULFIDE SULFUR

**Apparatus.** **Gas Generating Flask.**—Connect a dry 500-ml. boiling flask with a long-stem separatory funnel and a small connecting bulb by means of a rubber stopper. Bend the stem of the funnel so that it will not interfere with the con-

necting bulb, adjust the stem so that the lower end is close to the bottom of the flask, and connect the opening of the funnel with a source of compressed air. Connect the bulb with an L-shaped glass tube and a straight glass tube about 20 cm. in length. Insert the straight glass tube in a tall-form, 400-ml. beaker. A three-neck distilling flask with a long glass tubing in the middle opening, placed between the source of compressed air and the funnel, is a convenient aid in the regulation of the air flow. If the air contains  $\text{H}_2\text{S}$  or  $\text{SO}_2$ , a solution of lead acetate or some other suitable absorbent shall be used in the bottle. Rubber used in the apparatus shall be of a pure-gum grade low in sulfur and shall be cleaned with warm  $\text{HCl}$ .

**Reagents. Starch Solution.**—To 100 ml. of boiling water, add a cool suspension of 1 g. of soluble starch in 5 ml. of water and cool. Add a cool solution of 1 g. of  $\text{NaOH}$  in 10 ml. of water, then 3 g. of  $\text{KI}$ , and mix thoroughly.

**Standard Potassium Permanganate Solution, 0.03 N.**—Prepare a solution of  $\text{KMnO}_4$  on the basis of 0.94 g. per liter. The solution should not be filtered through any filter containing organic matter. It is most convenient to siphon off clear solution without disturbing the sediment on the bottom of the bottle. Standardize the solution against about 0.15 g. of sodium oxalate oxidimetric standard furnished by the National Bureau of Standards (standard sample No. 40) according to the directions furnished with the sodium oxalate.

**Standard Sodium Thiosulfate Solution, 0.03 N.**—Prepare a solution of  $\text{Na}_2\text{S}_2\text{O}_3$  on the basis of 7.4 g. of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  per liter.

**Standard Potassium Iodate Solution, 0.03 N.**—Prepare a solution of  $\text{KIO}_3$  and  $\text{KI}$  on the basis of 1.12 g. of  $\text{KIO}_3$  and 12 g. of  $\text{KI}$  per liter. Standardize the solution as follows: To a cool solution of 1 g. of  $\text{KI}$  in 300 ml. of water and 10 ml. of  $\text{HCl}$  in a 500-ml. flask, add about 25 ml. of the standard  $\text{KMnO}_4$  solution, swirl the solution gently, stopper the flask, and let stand for 5 minutes. Titrate the liberated iodine with the standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution until the color nearly fades. Add 2 ml. of the starch solution, continue the titration until the blue color is destroyed, and back-titrate with the standard  $\text{KMnO}_4$  solution until the blue color just reappears. Repeat the titration with the  $\text{KIO}_3$  solution substituted for the  $\text{KMnO}_4$  solution. Calculate the sulfur equivalent of the standard  $\text{KIO}_3$  solution in grams per milliliter as follows:

$$E = \frac{A \times C \times G \times 0.2392}{B \times D \times F}$$

where  $E$  = sulfur equivalent of the  $\text{KIO}_3$  solution in grams per milliliter

$A$  = grams of  $\text{Na}_2\text{C}_2\text{O}_4$  used in the standardization of the  $\text{KMnO}_4$  solution

$B$  = milliliters of  $\text{KMnO}_4$  solution required by  $A$

$C$  = milliliters of  $\text{KMnO}_4$  solution used in the standardization of the  $\text{KIO}_3$  solution

$D$  = milliliters of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required by  $C$

$F$  = milliliters of  $\text{KIO}_3$  solution used in the standardization of the  $\text{KIO}_3$  solution

$G$  = milliliters of  $\text{Na}_2\text{S}_2\text{O}_3$  solution required by  $F$

**NOTE.**—One milliliter of a normal solution of  $\text{KMnO}_4$  or  $\text{KIO}_3$  is equivalent to 0.06701 g. of  $\text{Na}_2\text{C}_2\text{O}_4$  or 0.01603 g. of sulfur. The number 0.2392 is obtained by dividing 0.01603 by 0.06701. The  $\text{KIO}_3$  and  $\text{KMnO}_4$  solutions should be standardized frequently, but, as the  $\text{Na}_2\text{S}_2\text{O}_3$  solution is more stable, the  $\text{KIO}_3$  solution may sometimes be standardized against the  $\text{Na}_2\text{S}_2\text{O}_3$  solution alone and without the last values of  $A$ ,  $B$ ,  $C$ , and  $D$  being changed.

**Stannous Chloride Solution.**—To 10 g. of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in a small flask, add 7 ml. of  $\text{HCl}$  (1:1), warm the mixture gently until the salt is dissolved, cool the solution, and add 95 ml. of water. This solution should be prepared as needed, as the salt tends to hydrolyze.

**Ammoniacal Zinc Sulfate Solution.**—Dissolve 50 g. of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in 150 ml. of water and 350 ml. of  $\text{NH}_4\text{OH}$ . Filter the solution after allowing it to stand at least 24 hours.

**Ammoniacal Cadmium Chloride Solution.**—Dissolve 15 g. of  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$  in 150 ml. of water and 350 ml. of  $\text{NH}_4\text{OH}$ . Filter the solution after allowing it to stand at least 24 hours.

**Procedure.**—Place 15 ml. of the ammoniacal  $\text{ZnSO}_4$  solution (NOTE 1) and 285 ml. of water in the beaker. Put 5 g. of the sample (NOTE 2) and 10 ml. of water in the flask and shake the flask gently to wet and disperse the cement completely. This step and the following one should be performed rapidly to prevent the setting of the cement. Connect the flask with the funnel and bulb. Add 25 ml. of the  $\text{SnCl}_2$  solution through the funnel and shake the flask. Add 100 ml. of  $\text{HCl}$  (1:3) through the funnel and shake the flask. During these shakings, keep the funnel closed and the delivery tube in the ammoniacal  $\text{ZnSO}_4$  solution. Connect the funnel with the source of compressed air, open the funnel, start a slow stream of air, and heat the flask and contents slowly to boiling. Continue the boiling gently for 5 or 6 minutes, cut off the heat, and continue the passage of air for 3 or 4 minutes. Disconnect the delivery tube and leave it in the solution for use as a stirrer. Cool the solution to  $20^\circ$  to  $30^\circ\text{C}$ . (NOTE 3), add 2 ml. of the starch solution and 40 ml. of  $\text{HCl}$  (1:1), and titrate immediately with the standard  $\text{KIO}_3$  solution until a persistent blue color is obtained (NOTE 4).

NOTE 1.—In general, the  $\text{ZnSO}_4$  solution is preferable to the  $\text{CdCl}_2$  solution because  $\text{ZnSO}_4$  is more soluble in  $\text{NH}_4\text{OH}$  than is  $\text{CdCl}_2$ . The  $\text{CdCl}_2$  solution may be used when there is doubt as to the presence of a trace of sulfide sulfur, as the yellow  $\text{CdS}$  facilitates the detection of a trace.

NOTE 2.—If the content of sulfur exceeds 0.20 or 0.25%, a smaller sample should be used so that the titration with the  $\text{KIO}_3$  solution will not exceed 25 ml.

NOTE 3.—The cooling is important, as the end point is indistinct in a warm solution. A part of the  $\text{NH}_4\text{OH}$  is lost during the distillation and the remaining  $\text{NH}_4\text{OH}$  reacts with acid, raising the temperature of the solution a few degrees without rendering the end point uncertain.

NOTE 4.—If the content of sulfur is appreciable but not approximately known in advance, the result may be low due to the loss of  $\text{H}_2\text{S}$  during a slow titration. In such a case the determination should be repeated with the titration carried out more rapidly.

**Blank.**—Make a blank determination, following the same procedure and using the same amounts of reagents, and correct the results obtained in the analysis accordingly.

**Calculation.**—Calculate the percentage of sulfur (NOTE 5) as follows:

$$\text{Sulfur, \%} = EV \times 20$$

where  $E$  = sulfur equivalent of the  $\text{KIO}_3$  solution in grams per milliliter

$V$  = milliliters of  $\text{KIO}_3$  solution required by the sample

20 = 100 divided by the weight of sample used (5 g.)

NOTE 5.—Sulfites, thiosulfates, and other compounds intermediate between sulfides and sulfates are assumed to be absent. If such compounds are present, they may cause an error in the determination.

## DETERMINATION OF LOSS ON IGNITION

**Procedure.**—Heat 1 g. of the sample in a weighed, covered platinum crucible of 20- to 25-ml. capacity, as follows, using either Method A or B as specified.

**NOTE.**—These methods are not considered suitable for the determination of the loss of volatile matter on ignition of portland blast-furnace slag cement and of slag cement. A method suitable for such cements is described in Section 19 of the Tentative Methods for Chemical Analysis of Portland Cement (ASTM C114-58T).

**Method A.**—Place the crucible in a hole in an asbestos board clamped horizontally, so that about three-fifths of the crucible projects below the board. Ignite at a full red heat ( $900^{\circ}$  to  $1000^{\circ}\text{C}.$ ) until constant weight is obtained. Allow a minimum of 15 minutes for the initial heating period and 5 minutes for all subsequent periods. Take care to wipe off particles of asbestos that may adhere to the crucible when withdrawn from the hole in the board. Greater neatness and shortening of the time of heating may be secured by making a hole to fit the crucible in a circular disc of sheet platinum and placing this disc over a somewhat larger hole in an asbestos board.

**Method B.**—Ignite the crucible and its contents to constant weight in a muffle furnace at a temperature of  $950^{\circ} \pm 50^{\circ}\text{C}.$  Allow a minimum of 15 minutes for the initial heating period and 5 minutes for all subsequent periods.

**Calculation.**—Calculate the percentage of loss on ignition to the nearest 0.1 by multiplying the loss in weight in grams by 100.

## DETERMINATION OF SODIUM AND POTASSIUM OXIDE

The American Society for Testing and Materials Standard Method as described in C114-58, Sections 21 through 23, and commonly referred to as the "J. L. Smith Method" is a complicated procedure requiring several days for completion. It is now seldom used except for such projects as the development of primary standards as specified in the flame photometric methods for the determination of sodium and potassium oxide. Flame photometers are comparative instruments and are subject to interferences from other elements that may be contained in the unknowns; consequently it is vitally important that primary standards, based on sound gravimetric procedures, be available for calibration and performance tests.

The method detailed below will be the current ASTM Tentative Standard C114-58T, with modifications that will be similar to Federal Test Method Standard No. 158.

SODIUM OXIDE AND POTASSIUM OXIDE BY FLAME PHOTOMETRY,  
USING THE DIRECT-INTENSITY METHOD

**Apparatus.**—The flame photometer consists essentially of a solution atomizer, a Meker-type burner operating on a mixture of propane gas and filtered air containing the atomized solution, a light slit and light-collimating system between the flame and light-dispersing prism or prisms, followed by a condensing lens and a movable light slit whose position is indicated on a wavelength scale and which passes a selected wave band of refracted light to a photoelectric cell. The light beam is interrupted periodically to cause an a-c output of the photocell current. The current generated by the cell is amplified and its intensity is measured by meter deflection and compared with that of similar currents set up by known concentrations of elements.

The flame photometer shall be mounted in a suitable cabinet and shall include the following features and accessories:

**Air Supply.**—Compressed air shall be supplied to the apparatus through a dust filter, a liquid trap, and a pressure-regulating and reducing valve capable of delivering air to the apparatus at the rate of 2 cu. ft. per minute and at a constant pressure within the range from 8 to 15 psi., with a maximum deviation of  $\pm 0.1$  psi. from the selected pressure.

**Gas Supply.**—Compressed propane gas or commercial "bottled gas" shall be supplied to the apparatus through a pressure-regulating and reducing valve at a constant pressure within the range from 2 to 10 psi. and with a maximum deviation of  $\pm 0.1$  psi. from the selected pressure.

**Solution Atomizer Assembly.**—The solution atomizer shall be of acid-resistant glass construction and shall be capable of atomizing solutions at a rate ranging from 10 to 25 ml. per minute with an accuracy of  $\pm 1$  ml. at any point within this range when air at a pressure of 10 psi. is supplied to the air port. The atomizer shall be easily accessible for cleaning. The vessel receiving the atomized solution shall also be of glass of such construction that large droplets of solution are led to a drain. The finer droplets suspended in air shall be led to the air port of the burner through a tube having a smooth internal bore of approximately  $\frac{3}{8}$  in.

**Gas Burner Assembly.**—The gas burner shall be of the Meker type designed for proper combustion of propane gas with air. The grid and grid holder shall be made of a metal not easily corrodible by hydrochloric acid solution and, together with the burner, shall be easily detachable for cleaning purposes. The burner shall be provided with a means of adjusting the air-gas ratio to permit recommended flame characteristics. A heat-resistant colorless glass chimney to ensure steady operation shall be provided, together with a suitable support.

**Optical System.**—The monochromator shall consist of an entrance slit of suitable dimensions, a system of lenses and prisms for collimating, dispersing, and focusing the light beam, an exit slit and wavelength selector, and a photocell. At a point in the light path between the flame source and the first lens, there shall be a mechanical means (such as a reed vibrator or motor-driven chopper disc) for interrupting the radiation at a constant frequency to provide an a-c signal from the photocell.

**Electric Current Supply.**—The electric current supply shall be 110- to 115-v., 60-cycle, a-c current obtained from a suitable regulator capable of maintaining voltage with an accuracy of  $\pm 1$  v.

**Electric Circuit.**—The electric circuit shall be an a-c amplifier operating at the radiation modulation frequency. The amplifier shall have such gain and stability that the amplified signal, after synchronous rectification and filtering, can be read on a standard meter. The gain control of the amplifier shall be regulated by a coarse and fine adjustment.

**Indicating Meter.**—The meter shall be a standard panel meter of 100 scale divisions readable and reproducible to  $\frac{1}{2}$  division.

**NOTE.**—The type of flame photometer as described has been found to be generally satisfactory; however, other flame photometers, together with suitable procedures, may be used provided the equipment meets the following performance tests: The equipment must be capable of obtaining values for sodium oxide and potassium oxide on samples such as National Bureau of Standards Sample No. 177 within  $\pm 0.02$  percentage points of the certified values.

**Reagents. Calcium Chloride Stock Solution.**—Add 300 ml. of water to 112.5 g. of  $\text{CaCO}_3$  (NOTE) in a 1500-ml. beaker. While stirring, slowly add 500 ml. of HCl (sp. gr. 1.18). Cool the solution to room temperature, filter into a 1-liter

volumetric flask, dilute to the mark, and mix thoroughly. This solution contains the equivalent of 63,000 p. p. m. (6.3%) of CaO.

NOTE.—The calcium carbonate shall be A.C.S. "low-alkali"  $\text{CaCO}_3$ , carrying a specification limit of 0.02% total alkalis as sulfate. The purchaser should assure himself that this specification is met.

**Sodium-Potassium Chloride Stock Solution.**—Dissolve 1.8858 g. of NaCl and 1.5830 g. of KCl (previously dried at 105° to 110°C. for several hours) in water, dilute to 1 liter in a volumetric flask, and mix thoroughly. This solution contains the equivalent of 1000 p. p. m. (0.10%) each of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ .

TABLE 29-2. STANDARD SOLUTIONS

Designation of Standard		Composition of Standard		Final Volume of Solution, ml.
Solution No.	Concentration of Alkali (Expressed as $\text{Na}_2\text{O}$ or $\text{K}_2\text{O}$ ), p. p. m.	$\text{CaCl}_2$ Stock Solution, ml.	NaCl-KCl Stock Solution, ml.	
1	100	200	200	2000
2	75	100	75	1000
3	50	100	50	1000
4	25	100	25	1000
5	10	100	10	1000
6	0	100	0	1000
7	100	0 <sup>a</sup>	100	1000

<sup>a</sup> The calcium-free solution is for use only in determining the correct positions of the wave length selector for maximum responses to  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ .

**Standard Solutions.**—Prepare the standard solutions prescribed in Table 29-2. The required volume of NaCl-KCl stock solutions shall be measured in calibrated pipets or burets and the  $\text{CaCl}_2$  stock solutions may be measured in a graduated cylinder. Each solution shall be placed in a volumetric flask, diluted to the volume indicated in Table 29-2 and mixed thoroughly. The solutions shall be stored in bottles of acid-resistant glass with ground-glass or rubber stoppers.

**Calibration of Apparatus.** (a) Warmup of Apparatus and Adjustment of Flame.—Turn on the electric current (NOTE 1). Adjust the air pressure to approximately 10 psi. and the gas pressure to approximately 5 psi., and light the burner. After a few minutes, place the chimney in a vertical position, with its bottom edge centered and approximately  $\frac{1}{8}$  to  $\frac{1}{4}$  in. below the top of the burner. Then adjust the air-gas ratio to give a faintly visible flame 5 to 6 in. high and with  $\frac{1}{8}$  in. cones over the burner grid. These cones should be uniform, quiet, and of blue or greenish-blue color. Allow approximately 30 minutes after the current and gas are turned on for warmup of the system before using the apparatus.

NOTE 1.—Under humid conditions it is often advisable to leave the electrical circuit on continuously, although a chopper motor should be disconnected to avoid excessive wear. With the vibrator the whole system can be left on. This keeps the temperature slightly elevated to prevent moisture condensation.

(b) **Calibration Procedure.**—(1) If the apparatus is equipped with cells for the determination of alkalis by the internal-standard method, set and leave the internal-standard dial at zero. Turn the meter zero-adjustment knob until the panel meter reads zero.

(2) Find the correct position on the wavelength dial for the element to be determined by pouring into the atomizer (NOTE 2) some of the standard calcium-free solution (No. 7, Table 29-2) and moving the selector slowly back and forth on each side of the indicated wavelength for the element until the point for maximum deflection of the meter is noted. Set the wavelength selector at this point. The coarse and fine gain controls are used to adjust the deflections to the range 90 to 100.

NOTE 2.—The atomizer shall be rinsed with each solution prior to taking readings on that solution.

(3) Pour the 100-p. p. m. standard calcium-alkali solution (No. 1) into the atomizer and adjust the coarse and fine gain controls until the meter reads 100. Then pour the standard alkali-free solution (No. 6) into the atomizer and turn the zero-adjustment knob until the meter reads zero. Repeat these two operations until no appreciable adjustment is necessary in going from one to the other.

(4) Next, pour into the atomizer the 75-p. p. m. standard solution (No. 2) and note the meter reading. Check the zero reading with standard alkali-free solution (No. 6). Return to the 100-p. p. m. standard solution (No. 1). These last two readings serve to evaluate the reading for the 75-p. p. m. solution. If they are within one scale division of zero and 100, respectively, the meter reading obtained for the 75-p. p. m. solution can be considered correct. If either the zero or 100-p. p. m. reading are not within one scale division of zero and 100, respectively, then the previously obtained meter reading for the 75-p. p. m. solution (No. 2) shall be rejected. In the latter event, step (3) shall be repeated and another reading taken for the 75-p. p. m. solution. Only when the zero and 100-p. p. m. readings are in proper relation both before and after taking readings on an intermediate standard can the intermediate standard readings be taken as accurate.

(5) In a similar manner, determine and record meter readings for the 50-, 25-, and 10-p. p. m. standard solutions (Nos. 3, 4, and 5), comparing them with the zero and 100-p. p. m. solutions as in step (4).

(6) Plot calibration curves for each oxide using cross-section paper of such type that each division on the ordinate represents a meter reading of one, and each division on the abscissa represents a concentration of 1 p. p. m. or 0.01% of alkali oxide (NOTES 3 and 4).

NOTE 3.—Since the cement to be analyzed is made up with 1 g. of cement in 100 ml. of solution, 1% of  $\text{Na}_2\text{O}$  in the cement is equivalent to 1 part of  $\text{Na}_2\text{O}$  in 10,000 parts of the solution. One part in 10,000 is 100 p. p. m.; hence the 100-p. p. m.  $\text{Na}_2\text{O}$  standard solution (which contains 0.01%  $\text{Na}_2\text{O}$  as  $\text{NaCl}$ ) is equivalent, in the determination, to a cement containing 1.0% of  $\text{Na}_2\text{O}$ . Likewise, the 10-p. p. m. standard solution is equivalent to a cement containing 0.1% of  $\text{Na}_2\text{O}$ , and the other standard solutions fall in their equivalent positions.

NOTE 4.—It is recommended that each laboratory using this method keep available two or more samples of cement whose  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  contents have been carefully determined by standard gravimetric procedures. Analyses made on these samples will be of value as



a check on each new set of standard solutions and will serve to assure the operator of the proper functioning of the apparatus.

**Procedure. Solution of the Cement.**—Place 1.000 g. of the cement in a 150- to 250-ml. beaker and disperse with 10 to 25 ml. of water, using a swirling motion of the beaker. While still swirling, add 5 ml. of HCl (sp. gr. 1.18) all at once. Dilute immediately to 50 ml. with water. Break up any lumps of cement remaining undispersed with a flat-end stirring rod. Digest on a steam bath or hot plate for 15 minutes and filter through a medium-texture paper into a calibrated 100-ml. volumetric flask. Wash the beaker and paper thoroughly with water. Cool the contents of the flask to room temperature, dilute to 100 ml., and mix the solution thoroughly.

**Determination of  $\text{Na}_2\text{O}$ .**—Warm up the apparatus and adjust the flame as described under paragraph (a) of Calibration of Apparatus. Find the point of maximum response to  $\text{Na}_2\text{O}$  on the wavelength scale by use of the standard calcium-free solution (No. 7) in the atomizer and set the wavelength selector at this point as described under paragraph (b), step (2) of Calibration of Apparatus. Then with alternate use of the standard alkali-free solution (No. 6) and the 100 p. p. m. standard calcium-alkali solution (No. 1), set the zero-adjustment knob and coarse and fine gain controls until the meter reading consistently changes from zero to 100 as the alkali-free solution is replaced with the 100-p. p. m. solution.

Following these adjustments, run cement solution through the atomizer and note its meter reading. Select the standard solution closest to the cement solution in  $\text{Na}_2\text{O}$  content and observe its meter reading. This value should agree within one division on the meter scale with the value established during calibration of the apparatus. If it does not, reset the meter needle to the original calibration point by use of the gain control. Also, if necessary, readjust the zero point with the standard alkali-free solution (No. 6) in the atomizer. Finally, alternate the use of the unknown solution and the closest standard solution until readings for the unknown agree within one division on the meter scale, and readings for the standard similarly agree with the calibration point. Record the average of the last two meter readings obtained for the unknown solution.

**Determination of  $\text{K}_2\text{O}$ .**—Determine  $\text{K}_2\text{O}$  as directed for  $\text{Na}_2\text{O}$  in paragraph (b), except that the wavelength selector shall be set at the point of maximum response to  $\text{K}_2\text{O}$  by use of the standard calcium-free solution (No. 7).

**Calculations and Report.**—Using the recorded average of meter reading for  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  in the unknown sample, read the percentage of each oxide from its respective calibration curve. Report each oxide to the nearest 0.01%.

#### DETERMINATION OF WATER-SOLUBLE ALKALI

Refer to ASTM C114-58, Section 23.

#### DETERMINATION OF PHOSPHORUS PENTOXIDE

Refer to ASTM C114-58, Section 24.

#### DETERMINATION OF MANGANIC OXIDE

Refer to ASTM C114-58, Section 26.

#### DETERMINATION OF CHLOROFORM-SOLUBLE ORGANIC SUBSTANCES

Refer to ASTM C114-58, Section 29.

## DETERMINATION OF INSOLUBLE RESIDUE

**Procedure.**—To 1 g. of the sample (NOTE 1) add 25 ml. of cold water. Disperse the cement in the water and, while swirling the mixture, quickly add 5 ml. of HCl. If necessary, warm the solution gently and grind the material with the flattened end of a glass rod for a few minutes until it is evident that decomposition of the cement is complete (NOTE 2). Dilute the solution to 50 ml. with hot water (near boiling) and heat the covered mixture rapidly to near boiling by means of a high-temperature hot plate. Then digest the covered mixture for 15 minutes at a temperature just below boiling (NOTE 3). Filter the solution into a 400-ml. beaker, wash the beaker, paper, and residue thoroughly with hot water, and reserve the filtrate for the sulfur trioxide determination, if desired (NOTE 4). Transfer the filter paper and contents to the original beaker, add 100 ml. of hot (near boiling) NaOH solution (10 g. per liter) and digest at a temperature just below boiling for 15 minutes. During the digestion, occasionally stir the mixture and attempt to macerate the filter paper. Acidify the solution with HCl using methyl red as the indicator and add an excess of four or five drops of HCl. Filter and wash the residue at least 14 times with hot  $\text{NH}_4\text{NO}_3$  solution (20 g. per liter), making certain to wash the entire filter paper and contents during each washing. Ignite the residue in a tared crucible at  $900^\circ$  to  $1000^\circ\text{C}.$ , cool in a desiccator, and weigh.

This method or any other method designed for the estimation of acid-insoluble substance in any type of cement is empirical, because the amount obtained depends on the reagents and the time and temperature of digestion. If the amount is large, there may be a little variation in duplicate determination. The directions should be followed closely in order to reduce the variation to a minimum. When the method is used on blended cement, the decomposition in acid is considered to be complete when the portland cement clinker is decomposed completely. An  $\text{NH}_4\text{NO}_3$  solution is used in the final washing to prevent finely ground insoluble material from passing through the filter paper.

NOTE 1.—If sulfur trioxide is to be determined by turbidimetry (ASTM C114-58, Section 44), it is permissible to determine the insoluble residue on a 0.5-g. sample. In this event, the percentage of insoluble residue should be calculated to the nearest 0.01 by multiplying the weight of residue obtained by 200. However, the cement should not be rejected for failure to meet the insoluble residue requirement unless a 1-g. sample has been used.

NOTE 2.—If a sample of portland cement contains an appreciable amount of manganic oxide, there may be brown compounds of manganese which dissolve slowly in cold diluted HCl but rapidly in hot HCl in the specified strength. In all cases, dilute the solution as soon as decomposition is complete.

NOTE 3.—In order to keep the solutions closer to the boiling temperature, it is recommended that these digestions be carried out on an electric hot plate rather than on a steam bath.

NOTE 4.—Continue with the sulfur trioxide determination (as described on p. 1060, or by ASTM C114-58, Section 16 or 44) by diluting to 250 or 200 ml. as required by the appropriate method.

**Blank.**—Make a blank determination, following the same procedure and using the same amounts of reagents, and correct the results obtained in the analysis accordingly.

**Calculation.**—Calculate the percentage of the insoluble residue to the nearest 0.01 by multiplying the weight in grams of the residue (corrected for the blank) by 100.

## DETERMINATION OF FREE CALCIUM OXIDE IN PORTLAND CEMENT AND CLINKER

This method, which has been standardized by the ASTM under designation C114-58T, covers a detailed procedure for the determination of free calcium oxide in fresh portland cement clinker. When it is applied to portland cement or aged clinker, the possibility of the presence of calcium hydroxide should be kept in mind, as this method does not differentiate between free calcium oxide ( $\text{CaO}$ ) and free calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ).

This method is based on the solution of free calcium oxide in a hot solution of glycerol and alcohol and the subsequent titration of the dissolved lime with an alcoholic solution of ammonium acetate.

**Apparatus.** Boiling Assembly.—It is recommended that all sections of the boiling assembly have standard-taper, interchangeable ground-glass joints, although connections with clean, tight-fitting rubber stoppers are permissible. The flask used for boiling the sample and solution shall be a flat-bottom, short-neck boiling flask or Erlenmeyer flask of 200- or 250-ml. capacity. The reflux condenser shall have a length of at least 300 mm. if water-cooled or 500 mm. if air-cooled.

**Buret.**—A buret having a 10-ml. capacity and graduated in units of not more than 0.05 ml. is required. A refilling type of semimicro buret with a 100-ml. reservoir is recommended and the air entering the reservoir should pass through a protective tube containing soda-asbestos (Ascarite), and anhydrous calcium sulfate (Drierite), or other suitable agents, for removal of carbon dioxide and moisture.

**Reagents.**—It is essential that the reagents and subsequent solutions be protected from moisture and carbon dioxide.

**Ammonium Acetate.**—Ammonium acetate usually is damp upon receipt or after laboratory storage and must be dried before use. Desiccation drying is recommended for a period of not less than two weeks, using anhydrous calcium sulfate (Drierite), or other drying agents of equal efficiency. If the ammonium acetate appears damp after this storage period, the presence of free acetic acid is noted, and a fresh supply of ammonium acetate must be used.

**Ammonium Acetate, Standard Solution** (1 ml. = 0.005 g.  $\text{CaO}$ ).—Prepare a standard solution of ammonium acetate ( $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ) by dissolving 16 g. of desiccated ammonium acetate in 1 liter of ethanol in a dry, clean, stoppered bottle.

Standardize this solution as follows: Ignite approximately 0.1 g. of calcium carbonate ( $\text{CaCO}_3$ ) or calcium oxalate ( $\text{CaC}_2\text{O}_4$ ) in a platinum crucible at  $900^\circ$  to  $1000^\circ\text{C}$ ., cool the contents in a desiccator, and weigh to the nearest 0.0001 g. to constant weight. The weighings shall be performed quickly to prevent absorption of water and carbon dioxide ( $\text{CO}_2$ ). Immediately transfer the  $\text{CaO}$  without grinding to a clean, dry, 200- or 250-ml. Erlenmeyer flask and reweigh the empty crucible to determine the weight of  $\text{CaO}$  used to the nearest 0.0001 g. Add to the flask 60 ml. of glycerol-ethanol solvent and a few glass beads to ensure vigorous boiling and complete agitation without bumping when heat is applied. Disperse the  $\text{CaO}$  in the solution by shaking the flask, and attach a reflux condenser. Boil the mixture. The ebullition should be positive but not so violent as to cause bumping or excessive evaporation. Then remove the condenser and immediately titrate the solution, while near boiling, with the standard ammonium acetate solution. Replace the condenser and boil the solution again. Repeat the titration at intervals. Shake the flask frequently between titrations to shorten the time required for the boiling. In general, the titration intervals may be 20 minutes, but they will chiefly depend on the rapidity of the dissolution of  $\text{CaO}$ . (*Caution.* See

NOTE 1.) The titration is complete when the pink color does not appear in the solution during continuous boiling for 1 hour (NOTE 2). If the end point is accurately determined, the solution will turn pink upon cooling, since the end point will not be the same for a hot and cold solution. This can serve as evidence that the end point has not been greatly exceeded.

Calculate the CaO equivalent of the ammonium acetate solution in grams per milliliter by dividing the weight of CaO used by the volume of solution required.

NOTE 1. *Caution.*—The use of an open gas flame for boiling the solvent-sample mixture presents a fire hazard and therefore is not recommended.

NOTE 2.—Titrations should be conducted at 5-minute intervals for the first 20 minutes to prevent the formation of crystals (probably calcium glyceride) which dissolve slowly and increase the time required for the completion of the titration. Thereafter, the color of the solution should be used as a guide for the titration interval.

**Ethanol.**—Absolute ethanol is preferred but may be replaced by anhydrous ethanol denatured according to Formula No. 3a or 2b of the U. S. Bureau of Internal Revenue. The Formula 3a alcohol is 95% ethanol and 5% methanol, and the Formula No. 2b alcohol is 99.5% ethanol and 0.5% benzol.

**Glycerol.**—Water, although usually included by the manufacturer in the list of impurities on the label, is almost always present in glycerol. To ensure that the water content is under 5%, the specific gravity at 25/25°C. should be determined by means of a pycnometer and should be not less than 1.249.

**Glycerol-Ethanol Neutral Solvent.**—Prepare a solution consisting of 1 volume of glycerol and 5 volumes of ethanol. To a clean and thoroughly dried 2½-l. reagent bottle, add 1.0 pound of glycerol (360 ml.) and 1800 ml. of ethanol, using the ethanol as a rinse for the glycerol to ensure its complete transfer. To this mixture add 0.18 g. of phenolphthalein. Immediately stopper the bottle and warm slightly on a surface that is less than 120°C. Localized heating shall be prevented by frequent agitation, until the indicator is completely dissolved and thoroughly mixed.

The solvent mixture should be slightly alkaline, as indicated by a faint pink color when cooled to room temperature. If the mixture is colorless, add gradually a freshly prepared solution of sodium hydroxide (NaOH) in ethanol until a faint pink color is formed. An approved neutral point is reached when the faint pink color of 60 ml. of the solvent mixture disappears on boiling or can be dispelled by not more than 0.02 ml. (approximately one drop) of ammonium acetate solution (1 ml. = 0.005 g. CaO) (NOTE 3). If the color of the fresh solvent mixture is strong pink when cooled to room temperature, dispel the color by the addition of small increments of ammonium acetate solution until the faint pink color specified above is attained. If the solvent mixture becomes acid on standing, as indicated by the disappearance of the faint pink color, the alkalinity shall be readjusted to a faint pink color by the gradual addition of a freshly prepared solution of NaOH in ethanol.

NOTE 3.—The error resulting from an excess alkalinity equivalent to 0.02 ml. of ammonium acetate solution is only 0.01% of free CaO and may be disregarded.

**Procedure.**—Grind about 1.2 g. of the sample in an agate mortar for 5 minutes (NOTE 1). Weigh 1.000 g. of the finely ground sample into a clean, dry, 200- or 250-ml. Erlenmeyer flask, add 60 ml. of the glycerol-ethanol solvent and a few glass beads, and agitate to disperse the sample. Attach a reflux condenser and boil the solution in the flask on a hot plate or other suitable source of heat (*Caution*, see NOTE 1, above). Vigorous boiling is more essential with cement

than with the pure CaO used in standardizing the acetate solution and should be conducted so as not to necessitate shaking of the flask.

NOTE 1.—Thorough grinding of the sample is essential for proper exposure of the free lime grains that often are occluded in crystals of tricalcium silicate in the cement. However, exposure of the sample to the air must be kept at a minimum to prevent carbonation of the free lime. In particular, direct breathing into the sample must be avoided. The sample should be sufficiently fine to easily pass a No. 200 (74 micron) sieve, but actual sieving is not recommended. If the sample is not to be immediately tested, it must be kept in an airtight container to avoid unnecessary exposure to the atmosphere.

Remove the condenser, and immediately titrate the solution (NOTE 2), while near boiling, with ammonium acetate solution (1 ml. = 0.005 g. CaO). A slight pink color should remain after all but the final titration, since excess acetate solution reacts with the calcium aluminate and silicates present in the sample.

NOTE 2.—If it is necessary to leave the determination uncompleted, remove the flask from the condenser, titrate to a faint pink color, and stopper the flask tightly. When resuming the determination, boil the mixture before continuing the titration.

Attach the condenser, return the flask to the hot plate, and boil as before.

Repeat the titration and boiling cycles at periodic intervals, whenever the solution turns deeply pink or red, depending upon the speed of the solution of the free CaO. Titrations may be as frequent as 5 minutes, but should never exceed 20 minutes in the early stages. Continue titrations until the faint pink color from the previous titration does not deepen and the percentage of free CaO of the sample does not increase by more than 0.05 upon its discharge with the acetate solution after 2 hours of boiling. A strong daylight lamp with a reflector may be used as an aid in the discernment of the end point by matching the contents of the flask with similar contents in another flask that contains an excess of ammonium acetate.

Calculations.—Calculate the percentage of free CaO to the nearest 0.1 as follows:

$$\text{Free CaO, \%} = EV \times 100$$

where  $E$  = CaO equivalent of the ammonium acetate solution in grams per milliliter  
 $V$  = milliliters of ammonium acetate solution required by the sample

Precision.—Duplicate determinations by this method should agree within 0.20. The maximum permissible variation between the extreme values in triplicate determinations should be less than 0.30.

## OPTIONAL METHODS

The optional methods described in the following sections are provided for those who wish to use procedures shorter or more convenient than the preceding ones for the routine determination of certain components. In case of dispute, results must be obtained in accordance with the referee methods described above, and these results shall govern.

### DETERMINATION OF SILICON DIOXIDE (OPTIONAL METHOD)

*Procedure.*—Mix thoroughly 0.5 g. of the sample and about 0.5 g. of  $\text{NH}_4\text{Cl}$  in a 50-ml. beaker, cover the beaker with a watch glass, and add cautiously 5 ml. of  $\text{HCl}$ , allowing the acid to run down the lip of the covered beaker. After the

chemical action has subsided, lift the cover, add one or two drops of  $\text{HNO}_3$ , stir the mixture with a glass rod, replace the cover, and set the beaker on a water bath for 30 minutes (NOTE 1). During this time of digestion, stir the contents occasionally and break up any remaining lumps to facilitate the complete decomposition of the cement. Fit a medium-texture filter paper to a funnel, transfer the jelly-like mass of silicic acid to the filter as completely as possible without dilution, and allow the solution to drain through. Scrub the beaker with a rubber policeman and rinse the beaker and policeman. Wash the filter two or three times with hot  $\text{HCl}$  (1:99) and then with ten or twelve small portions of hot water, allowing each portion to drain through completely. Reserve the filtrate and washings for the determination of the ammonium hydroxide group (NOTE 2).

NOTE 1.—A hot plate may be used instead of a water bath if the heat is so regulated as to approximate that of a water bath.

NOTE 2.—Determine the ammonium hydroxide group by the procedure described under Determination of the Ammonium Hydroxide Group. Reserve the combined filtrates for the determination of  $\text{CaO}$  by either the referee or optional method.

Transfer the filter paper and residue to a weighed platinum crucible, dry, and ignite, at first slowly until the carbon of the paper is completely consumed without inflaming, and finally at  $1050^\circ$  to  $1100^\circ\text{C.}$  for 1 hour. Weigh the residue as  $\text{SiO}_2$  (NOTE 3).

NOTE 3.—If there is any doubt about the percentage of  $\text{SiO}_2$  meeting a specification requirement, the amount of impurities in the residue may be ascertained by treating the  $\text{SiO}_2$  with  $\text{HF}$  and  $\text{H}_2\text{SO}_4$  as directed under the referee method for silicon dioxide determination, p. 1055. However, the cement shall not be rejected for a low  $\text{SiO}_2$  content unless the determination is made according to the referee method.

Blank.—Make a blank determination, following the same procedure and using the same amounts of reagents, and correct the results obtained in the analysis accordingly.

Calculation.—Calculate the percentage of  $\text{SiO}_2$  to the nearest 0.1 by multiplying the weight in grams of  $\text{SiO}_2$  by 200 [100 divided by the weight of the sample used (0.5 g.)].

## DETERMINATION OF CALCIUM OXIDE (OPTIONAL METHOD)

**Reagents.** Standard Potassium Permanganate Solution, 0.18 N.—Prepare a solution of  $\text{KMnO}_4$  on the basis of 5.64 g. per l. The solution should not be filtered through any filter containing organic matter. It is most convenient to siphon off clear solution without disturbing the sediment on the bottom of the bottle. Standardize the solution against 0.7500 g. of sodium oxalate oxidimetric standard furnished by the National Bureau of Standards (standard sample No. 40) according to the directions furnished with the sodium oxalate. If the buret reading is 62.77 ml., the solution contains 0.0056357 g. of  $\text{KMnO}_4$  per milliliter, which is equivalent to exactly 0.005 g. of  $\text{CaO}$ . Because of impurities and deterioration, the reading in the standardization is usually not 62.77 ml. Calculate the  $\text{CaO}$  equivalent of the solution in grams per milliliter as follows:

$$E = \frac{0.31385}{V}$$

where  $E$  =  $\text{CaO}$  equivalent of the  $\text{KMnO}_4$  solution in grams per milliliter

$V$  = milliliters of  $\text{KMnO}_4$  solution required by 0.7500 g. of  $\text{Na}_2\text{C}_2\text{O}_4$

0.31385 = 62.77 multiplied by 0.005

**NOTE.**—The solution is intended to be equivalent to 0.005 g. of CaO per milliliter, or 1% CaO in a 0.5-g. sample for each milliliter. The numbers 0.0056357 and 62.77 are obtained as follows: 0.005 g. of CaO multiplied by the molecular ratio of  $2\text{KMnO}_4$  to  $5\text{CaO}$  gives 0.0056357 g. of  $\text{KMnO}_4$ ; 0.75 g. of  $\text{Na}_2\text{C}_2\text{O}_4$  multiplied by the molecular ratio of  $2\text{KMnO}_4$  to  $5\text{Na}_2\text{C}_2\text{O}_4$  gives 0.35375 g. of  $\text{KMnO}_4$ ; 0.35375 g. divided by 0.0056357 g. per ml. gives 62.77 ml.

**Procedure.** (See NOTE 1 of this section and NOTE 2, p. 1072).—Acidify the combined filtrates obtained in the determination of the ammonium hydroxide group (p. 1056) and, if necessary, evaporate to a volume of about 200 ml. Add 5 ml. of HCl, a few drops of methyl red indicator, and 30 ml. of warm ammonium oxalate solution (50 g. per l.). Heat the solution to  $70^\circ$  to  $80^\circ\text{C}$ ., and add  $\text{NH}_4\text{OH}$  (1:1) dropwise, while stirring, until the color changes from red to yellow. Allow the solution to stand without further heating for 1 hour (no longer), with occasional stirring during the first 30 minutes. Filter and wash the precipitate eight to ten times with hot water. The total amount of water used in rinsing the beaker and washing the precipitate should not exceed 75 ml. Reserve the filtrate for the determination of MgO. Carefully open the filter paper and wash the precipitate into the beaker in which the precipitation was effected. Dilute to 200 ml., and add 10 ml. of  $\text{H}_2\text{SO}_4$  (1:1). Heat the solution to a temperature just below boiling, and titrate with the standard  $\text{KMnO}_4$  solution (NOTE 2) to a permanent pink color. Add the filter paper and macerate it. Continue the titration slowly until the pink color persists for 10 seconds.

**NOTE 1.**—If there is a possibility of there being enough manganese to cause the percentage of MgO, as determined by the following section, to exceed a specified limit, manganese may be eliminated from the filtrate before applying the optional method for CaO. Although the elimination may be made as directed on p. 1058, the cement shall not be rejected for exceeding a limit specified for MgO unless the determination of MgO is made according to the referee method.

**NOTE 2.**—The temperature of the standard  $\text{KMnO}_4$  solution should not vary from its standardization temperature so much as to cause a serious error in the determination of CaO. At ordinary room temperatures the volume of pure water changes to the extent of 0.01 to 0.04% for each degree Centigrade, depending on the temperature.

**Blank.**—Make a blank determination, following the same procedure and using the same amounts of reagents (NOTE 3), and correct the results obtained in the analysis accordingly.

**NOTE 3.**—When the amount of calcium oxalate is very small, its oxidation by  $\text{KMnO}_4$  is slow to start. Before the titration, add a little  $\text{MnSO}_4$  to the solution to catalyze the reaction.

**Calculation.**—Calculate the percentage of CaO to the nearest 0.1 as follows:

$$\text{CaO, \%} = EV \times 200$$

where  $E$  = CaO equivalent of the  $\text{KMnO}_4$  solution in grams per milliliter

$V$  = milliliters of  $\text{KMnO}_4$  solution required by the sample

200 = 100 divided by the weight of sample used (0.5 g.)

#### DETERMINATION OF MAGNESIUM OXIDE. OPTIONAL METHOD A (RAPID GRAVIMETRIC DETERMINATION)

**Procedure.**—Acidify the filtrate from the determination of CaO (preceding section) with HCl and evaporate by boiling to about 250 ml. Cool the solution to room temperature, and add 10 ml. of  $(\text{NH}_4)_2\text{HPO}_4$  (100 g. per l.) and 30 ml. of

$\text{NH}_4\text{OH}$ . Stir the solution vigorously during the addition of  $\text{NH}_4\text{OH}$  and then for 10 to 15 minutes longer. Let the solution stand for at least 8 hours in a cool atmosphere and filter. Wash the residue five or six times with  $\text{NH}_4\text{OH}$  (1:20) and ignite in a tared platinum or porcelain crucible, at first slowly until the filter paper is charred and then burned off, and finally at  $1050^\circ$  to  $1100^\circ\text{C}$ . for 30 to 45 minutes. Weigh the residue as  $\text{Mg}_2\text{P}_2\text{O}_7$ .

**Blank.**—Make a blank determination, following the same procedure and using the same amounts of reagents, and correct the results obtained in the analysis accordingly.

**Calculation.**—Calculate the percentage of  $\text{MgO}$  to the nearest 0.1 as follows:

$$\text{MgO, \%} = W \times 72.4$$

where  $W$  = grams of  $\text{Mg}_2\text{P}_2\text{O}_7$

72.4 = molecular ratio of  $2\text{MgO}$  to  $\text{Mg}_2\text{P}_2\text{O}_7$  (0.3620) divided by the weight of sample used (0.5 g.) and multiplied by 100

## RAPID METHOD FOR THE DETERMINATION OF CARBONATES IN RAW MATERIALS

**Procedure.**—Weigh out 0.500 g. of very finely ground sample into a 500-ml. Erlenmeyer flask. Add 60 ml. of 0.200  $N$  hydrochloric acid and boil for about 5 minutes, using a reflux condenser to prevent the loss of acid. Wash the condenser down and cool the flask in a stream of cold water. Add a few drops of 0.5% phenolphthalein indicator and titrate with 0.200  $N$  sodium hydroxide solution to the first pink coloration which may be momentary. Shake the flask vigorously during the titration and add the last portion of the alkali dropwise. Add  $x$  ml. excess of sodium hydroxide. If the content of magnesium is high and the red color fades rapidly, it may be necessary to add the excess alkali in several small amounts with boiling between additions until a permanent red color is obtained. See below in regard to the required amount of  $x$ . Call the total volume of sodium hydroxide  $s$ . Transfer the contents of the flask to a 200-ml. test tube, add the rinsings, and bring the volume to 100 ml. Heat the mixture to boiling and then allow it to stand until the precipitated magnesium hydroxide settles. If the precipitate is large, it may be necessary to filter it on a dry filter paper. Draw 50 ml. of the clear solution with a pipet. Put it in the original flask and titrate with the standard hydrochloric acid to the disappearance of the red color. Call the volume of acid used in this back titration  $h$ .

On the assumption that all the calcium and magnesium in the sample exist as carbonates, values are calculated thus:

$$\text{Per cent MgCO}_3 = 1.68(x - 2h)$$

$$\text{Per cent CaCO}_3 = 2.0(60 + 2h - s)$$

This assumption is generally applicable to high-grade limestones. Frequently raw materials used in cement manufacture contain insoluble compounds of calcium and magnesium and sometimes other interfering substances. In order to use this method on such material it may be necessary to establish correction factors by comparison of results obtained by this method and actual values in a series of reference samples of known composition.

If the content of magnesia is much lower than specification limits, the de-



termination may be omitted. It is important that the titration with sodium hydroxide from which the equivalent calcium carbonate is calculated be stopped at the first pink coloration. When magnesium carbonate is determined, its content decides the amount of excess sodium hydroxide ( $x$ ) to be used. It should be such as to make ( $h$ ) equal to 0.2 to 0.5 ml. If insufficient sodium hydroxide is used, magnesium may not be completely precipitated. If too much is used, calcium may be partially precipitated with magnesium hydroxide.

NOTE.—This method has been in general use for many years and, although it is not considered as possessing great accuracy, it has been useful for control purposes. (First published in Cement and Engineering News, March 1903, p. 35.)

## ANALYSIS OF RAW MATERIALS

Raw materials used in the manufacture of portland cement range from high calcium limestones through argillaceous limestones to clays and shales. Slags, various metamorphic, and even igneous rocks are sometimes used. Supplementary materials include iron ores, quartzite and kaolin. Gypsum is interground with the clinker to produce the finished product.

*Decomposition of Sample.*—A satisfactory method of decomposing a cement raw material is to sinter the material at a temperature of about  $1300^{\circ}\text{C}$ .

In order to make a suitable sinter it is necessary to have a  $\text{CaO/SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  (lime ratio) of about two or greater. In the event the lime ratio is much less than two, the mixture is liable to fuse and such a fusion is very difficult to remove from the crucible and dissolves slowly. To overcome this difficulty sufficient chemically pure calcium carbonate is added to produce a lime ratio of two or more. The exact weight of added calcium carbonate is necessary only when a determination of calcium is required. With some of the silicate rocks it may be necessary to reduce the sample weight to about 0.2 g. and add 0.8 to 1.0 g. of chemically pure calcium carbonate.

The accuracy of the method will be increased by the use of blank determinations. Where calcium carbonate is added, an equal amount is also used in the blank.

It is convenient to make a sinter in a platinum crucible at a final temperature of about  $1300^{\circ}\text{C}$ . It is important to note that the temperature should be started at about  $850^{\circ}\text{C}$ . and increased slowly to  $950^{\circ}\text{C}$ . (5 minutes), then rapidly to about  $1300^{\circ}\text{C}$ . to complete the sinter. The carbonates contained in the mixtures release carbon dioxide within the above temperature range. If the increase in temperature is too rapid, mechanical loss of sample may result.

The classic method which uses sodium carbonate for the decomposition of silicate rocks is time consuming and difficult. If accurate determinations are required, it is necessary to employ double evaporations and precipitations in order to avoid contamination by the large amount of sodium used in the decomposition.

*Solution of Sample.*—A sinter, if properly made, is easily removed from the crucible, and any material that adheres to the crucible may be removed with a few drops of hydrochloric acid. The sinter may then be dissolved in acid and analyzed by the methods used for portland cement. If the ammonium chloride method for determination of  $\text{SiO}_2$  is used, transfer the sinter to a 50-ml. beaker containing about 0.5 g.  $\text{NH}_4\text{Cl}$  and cover with a watch glass. Measure 5 ml. of  $\text{HCl}$  (sp. gr. 1.18) in a graduate. Add about 1 ml. of the acid to the crucible and warm if necessary to dissolve remnants of sinter from the crucible. During this

period cautiously add about 2 ml. of the acid to the beaker containing the sinter and allow to stand until chemical action has subsided. Transfer the acid and dissolved material from the crucible to the beaker. Rinse the crucible with the remaining acid, using about 1-ml. portions. The total acid used should be 5 ml. Add two drops of  $\text{HNO}_3$ , stir the mixture, and break up any lumps with a glass rod until the sinter is decomposed.

**Determination of Substances Present.**—Analyze the solution obtained above by the methods described, starting with Section 33 of ASTM C114-58 (optional methods described above) except for iron determination. Iron may be determined by fusing  $\text{R}_2\text{O}_3$  precipitate with  $\text{K}_2\text{S}_2\text{O}_7$ , cooling, and dissolving the fused mass and titrating with standard  $\text{K}_2\text{Cr}_2\text{O}_7$ . In case greater accuracy is desired, a separate sinter containing 0.5 to 1.0 g. of sample and five times its weight of iron-free  $\text{CaCO}_3$  is prepared. The sinter is then dissolved in hydrochloric acid, the silica removed by evaporation, and the ammonium hydroxide group precipitated with ammonia. The ammonium hydroxide group is then dissolved in  $\text{HCl}$ , reduced with stannous chloride, and finally titrated with standard potassium dichromate.

## DETERMINATION OF SODIUM AND POTASSIUM OXIDE IN RAW MATERIALS

**Decomposition of Sample.**—Weigh from 0.2000 g. to 1.000 g. of sample, depending on the alkali content of the material to be analyzed. Transfer to a platinum dish, add 5 ml. cool water. Stir the mixture with a platinum rod, add 5 ml.  $\text{HNO}_3$  (1:1), and continue the stirring until chemical action subsides. Add 5 ml.  $\text{HClO}_4$  and 12.5 ml.  $\text{HF}$  and mix thoroughly with the rod (NOTE 1). Remove the rod and rinse with water. Evaporate the solution to dryness or fumes of  $\text{HClO}_4$  (NOTE 2). Cool the dish, wash down sides with water and repeat the evaporation. Drive off excess  $\text{HClO}_4$  by increasing the temperature, but maintaining a temperature less than red heat. Cover the dish with a watch glass of heat-resistant glass, and convert the perchlorates to chlorides by using stronger heat but still avoiding red heat. The residue fuses to a brown mass and may glow from an exothermic reaction. After the reaction is complete, continue the heating for 1 to 2 minutes below red heat. Cool the dish and watch glass. Rinse the watch glass into a beaker. Add a little water to the dish, let the residue stand a few minutes to soften, and grind it with a glass rod or pestle to a smooth paste. Wash the contents into the beaker and dilute to 40 to 50 ml. The alkalis may then be extracted by leaching residue with hot water, and filter with the aid of suction.

From this point the alkalis may be determined gravimetrically by either ASTM C114-58, Sections 21 and 22, Sections 45, 46, or by flame photometer, ASTM C114-58T, Sections 15 through 18, p. 1063.

**NOTE 1. WARNING.**—If the material is known to contain, or suspected of containing, organic matter, destroy by spreading the sample in a thin layer in the platinum dish and igniting at  $600^\circ$  to  $700^\circ\text{C}$  for approximately 10 minutes.

**NOTE 2.**—The evaporation must be done carefully as the contents have a tendency to spatter if the heat is too great. Infrared reflector lamps, properly adjusted, may be used successfully.

## Chapter 30

# CHEMICAL ANALYSIS IN CLINICAL MEDICINE

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**Introduction.**—Many investigators have need of standard clinical laboratory methods for analysis of body materials, such as blood, urine, spinal fluid, and feces. The medical literature, as well as the chemical literature, contains information concerning multiple procedures and modifications of standard procedures. In this chapter we will present a few of the simple standard procedures that may be performed in the usual clinical laboratory. No attempt has been made to be completely inclusive. Certain procedures and modifications have been omitted for the sake of brevity.

The procedures are arranged in rough alphabetical order, according to the major constituent sought. Most of the procedures listed have been used in the clinical laboratory of Indiana University Medical Center for the diagnosis and treatment of patients; however, a few have been obtained by careful search of the literature. We have attempted to choose the simplest and most accurate method applicable to the routine clinical laboratory.

## AMINO ACIDS

(Whole Blood, Serum, Plasma, or Urine)

**Reagents.** Sodium  $\beta$ -Naphthoquinone-4-Sulfonate, 0.5%.—Dissolve 500 mg. in 100 ml. of water, add approximately 2 g. of activated charcoal and filter. This should be a pale yellow.

**Acetic Acid-Acetate Buffer.**—Mix 100 ml. of 50% acetic acid (50 ml. of glacial acetic acid plus 50 ml. of distilled water) with 100 ml. of 5% sodium acetate (5 g. of the trihydrate to 100 ml. with distilled water).

**Standard (10 mg. per 100 ml. Amino Acid N).**—Make up 187.8 mg. of proline and 112.8 mg. of glycine to 1 liter with 0.1 N HCl, containing 2 g. of benzoic acid.

**Tungstic Acid.**—Equal volumes of 0.15 N  $\text{H}_2\text{SO}_4$  and 2.2% sodium tungstate are mixed on the day of the test.

**Procedure.** Whole Blood, Plasma, and Serum.—Wash 0.05 ml. of whole blood, plasma, or serum into 0.2 ml. of water. Add 1.0 ml. of tungstic acid. Mix and

centrifuge at 2000 r.p.m. To a 1-ml. aliquot, in a tube with a mark at 2 ml., add one small drop of 0.1% phenolphthalein solution followed by 0.05 ml. of 0.5 N NaOH. The solution should be a definite pink. If necessary, add additional NaOH dropwise until pink. Now add 0.25 ml. of 2% borax solution. Mix. The pH should be approximately 9.3. Now add 0.1 ml. of the sodium  $\beta$ -naphthoquinone-4-sulfonate solution. Mix well, heat 10 minutes at 100°C. Cool to room temperature. Add 0.25 ml. of acetic acid-acetate buffer followed by 0.25 ml. of 4% sodium thiosulfate solution. Make up to 2 ml. (pH of final solution 4-5). Read the color at 480  $m\mu$  in the Beckman spectrophotometer, at 470  $m\mu$  in the Coleman spectrophotometer, or with the 47 filter for the Klett Summerson colorimeter.

The blank comprises a 1-ml. aliquot taken from a mix of 0.2 ml. of water and 1 ml. of tungstic acid, treated as the unknown aliquot; 0.05 ml. of the 10 mg. per 100 ml. amino acid nitrogen standard is used for the standard, and treated as for the unknown, adding to 0.2 ml. of water, 1 ml. of tungstic acid, etc.

**Calculation.**—

$$\frac{\text{Absorbance of unknown}}{\text{Absorbance of standard}} \times 10 = \text{mg. amino acid N per 100 ml.}$$

**NOTE.**—Sodium  $\beta$ -naphthoquinone-4-sulfonate will slowly decompose even in the dry state. Thus, the reagent may appear pink when made up. Filtering with charcoal removes the red color. The reagent is then stable in the refrigerator for weeks. The colors of the reaction will tend to fade after one-half hour and should be read before that time.

**Urine.**—For urine add 9 ml. of tungstic acid to 1 ml. of urine. Mix, filter or centrifuge and evaporate a portion of the filtrate to one-half its volume. This is done to hydrolyze the amides which are present in urine. Take a 0.5-ml. aliquot and dilute to 1 ml. with water. Proceed as for the blood aliquot. One milliliter of water is used as the blank aliquot; for the standard dilute 0.1 ml. to 1 ml. and proceed as for the blood aliquot. Calculations are the same as for blood. Certain therapeutic agents, such as the sulfa drugs, containing an amino group attached to a benzene ring will tend to interfere in this test.

**NOTE.**—Normal amino acid nitrogen values are of the order of 4.5 mg. per 100 ml. for plasma, 5.5 mg. per 100 ml. for whole blood, and 2 mg. per 100 ml. for spinal fluid; 24-hour urine samples contain approximately 100 mg. of free amino acids.

## AMMONIA

(Serum or Plasma)

**Reagents.** **Indicating Boric Acid.**—Add 10 g. of boric acid to 100 ml. of water. Add 1 ml. of 0.1% methyl red (100 mg. to 100 ml. in ethanol) and 8 ml. of 0.1% bromcresol green (100 mg. to 100 ml. in ethanol). Dilute to 1000 ml. and shake until dissolved.

**Ammonium Standard** (1  $\mu$ g. N per 100 ml.).—Dissolve 236 mg. of  $(\text{NH}_4)_2\text{SO}_4$  (dried in a desiccator) and make up to 500 ml. with water. This solution contains 100  $\mu$ g. N per ml. Take 1 ml. of this solution and make up to 100 ml. to make the 1  $\mu$ g. N per ml. solution.

**Procedure.**—Into the outer chamber of a Conway diffusion dish is placed 1 ml. of serum, or whole blood, in one pool. One milliliter of indicating boric acid is placed in the central compartment. Lifting the cover, 1 ml. of 45% potassium carbonate solution is placed in the outer chamber on the opposite side of the dish

from the pool of serum or blood. The cover is replaced, and the potassium carbonate solution is mixed with the serum by rotating the dish on a flat surface. Diffusion is allowed to take place for 20 minutes. The cover is removed. A small stirring bar is placed in the center compartment, and the dish is placed on a magnetic stirrer. The solution is titrated rapidly with an ultramicro buret with 0.001 N HCl solution.

**Calculations.**—A 0.1-ml. titration (100 divisions) is equivalent to 1.4  $\mu$ g. of nitrogen (140  $\mu$ g. per 100 ml. of ammonia nitrogen or 170  $\mu$ g. per 100 ml. of ammonia, when 1 ml. of serum is taken). A blank using 1 ml. of water instead of serum is run, and 1 ml. of a standard (1  $\mu$ g. N per ml.) is also analyzed. Titration of the blank is subtracted from the titration of the unknown and standard before calculation.

$$\frac{\text{Titration of unknown}}{\text{Titration of standard}} \times 100 = \mu\text{g. ammonia N per 100 ml.}$$

$$\text{Micrograms ammonia N per 100 ml.} \times \frac{17}{14} = \mu\text{g. ammonia per 100 ml.}$$

**NOTE.**—In the procedure the serum or plasma is made alkaline, the ammonia is allowed to diffuse into the acid and estimated as above. Since 93% of the  $\text{NH}_3$  will diffuse in 20 minutes, this time is used to avoid hydrolysis of ammonia-containing compounds with liberation of free ammonia. Some recommend a diffusion time of only 10 minutes. Twenty minutes is chosen because studies show this to be an optimum time to get over the maximum amount of ammonia with the minimum amount of hydrolysis. Titration must be rapid to obtain a sharp end point.  $\text{CO}_2$  from the air will interfere in the titration if done slowly. It is recommended that a hole 1 cm. in diameter be drilled in the cover and that this be covered with a coverslip during diffusion. The coverslip only is removed when titrating. The stirrer is a length of paper clip wire (2 cm.) encased in a close fitting melting-point tube sealed at both ends. A length of polyethylene tubing instead of the glass is also satisfactory.

**NOTE.**—Normal blood ammonia nitrogen values range from 50 to 70  $\mu$ g. per 100 ml. by this method. For cerebrospinal fluid the values range from 0 to 15  $\mu$ g. per 100 ml. of ammonia nitrogen.

## AMYLASE (DIASTASE)

(Serum, Urine, and Duodenal Contents)

**Reagents. Starch Solution.**—Weigh 1.5 g. of soluble starch into a small beaker. Add about 20 ml. of distilled water and prepare a paste. Add 50 ml. of distilled water to a small beaker, bring to boil and slowly add the starch paste with constant stirring. This should result in a clear solution; if not, discard and repeat the procedure. Cool and place in a 100-ml. graduate. Adjust volume to 70.0 ml. with distilled water. Add 30 ml. of 0.066 M phosphate buffer at a pH of 6.8. Final volume equals 100 ml. Autoclave for exactly 15 minutes at a pressure of 10 pounds. Use vaccine bottle with rubber stopper. (*Caution:* Insert 20-gauge needle in stopper when autoclaving. Take pressure up slowly and after the autoclaving period, release pressure slowly.)

**Sodium Chloride, Acid 1%.**—To a liter volumetric flask add 10 g. of sodium chloride, reagent grade, and 3 ml. of 0.1 N HCl; then dilute to the mark with distilled water.

**Procedure. Serum Amylase.**—Label three clean 15.0-ml. centrifuge tubes as follows: number 1 (test); number 2 (starch control); and number 3 (serum control).

When doing more than one determination only *one* starch control tube need be prepared. To each of the tubes, add the following reagents in the order prescribed (see tabulation below). Remove sufficient starch solution for all the tubes from the sterile vaccine bottle using a sterile needle and syringe. Place the starch in a tube and then pipet the exact amount to each centrifuge tube.

<i>Tube Number 1</i>	<i>Tube Number 2</i>	<i>Tube Number 3</i>
1. 5 ml. starch	5 ml. starch	5 ml. distilled water
2. 2 ml. acid chloride	2 ml. acid chloride	2 ml. acid chloride
3. Incubate in water bath at 37°C. for 5 minutes	Incubate in water bath at 37°C. for 5 minutes	Incubate in water bath at 37°C. for 5 minutes
4. 1 ml. serum	1 ml. distilled water	1 ml. serum (Control)
5. Incubate in water bath at 37°C. for 30 minutes	Incubate in water bath at 37°C. for 30 minutes	Incubate in water bath at 37°C. for 30 minutes
6. 1 ml. $\text{CuSO}_4$ , 5%	1 ml. $\text{CuSO}_4$ , 5%	1 ml. $\text{CuSO}_4$ , 5%
7. 1 ml. $\text{Na}_2\text{WO}_4$ , 10%	1 ml. $\text{Na}_2\text{WO}_4$ , 10%	1 ml. $\text{Na}_2\text{WO}_4$ , 10%

Stopper and mix thoroughly. Centrifuge for about 10 minutes at high speed (approximately 2000 r.p.m.). Disregard turbidity in tube number 2 after centrifuging. Determine reducing substance content of each supernatant fluid by the Somogyi-Nelson method for blood glucose, p. 1094, with the following exception: use *only 1 ml.* of the supernatant fluid plus 1 ml. of distilled water to give a total volume of 2 ml. If turbidity exists after the final color development in the Somogyi-Nelson glucose method, centrifuge before reading in the spectrophotometer.

**Calculations.**—Subtract total value in mg.% (milligrams per 100 ml.) of tubes number 2 and number 3 from tube number 1. This figure represents units of amylase, and can be reported as mg.% reducing substance or as units. Starch control should show minimal reducing substance, approximately 60 mg.% or less.

**Urinary Amylase Method.**—Test urine for glucose using Clinitest (Ames Laboratories). Adjust the pH of an aliquot of urine (25 to 50 ml.) to 6.8 to 7.2 by adding 20% sodium carbonate to alkalize or 10% potassium acid phosphate to acidify (use nitrazine paper as an indicator). If Clinitest is 2 plus or above, make a 1 to 2 dilution using normal saline. (Be sure to include this in the calculation.) Set up starch incubation and proceed as for serum amylase. Calculations are made as for serum method.

**Duodenal Contents.**—A 1:50 and 1:1000 dilution of the duodenal material is made as follows: (a) 1 ml. of duodenal contents is made up to 50 ml. by adding 10 ml. of buffer pH 7.2 and distilled water; (b) add 0.5 ml. of the 1:50 diluted sample to 9.5 ml. buffer to give a 1:1000 dilution. Proceed as for the serum amylase determination.

**NOTE.**—Normal values: 80 to 150 mg. reducing substance per 100 ml. of serum. This method of amylase determination is based on a modification of Somogyi's method of serum amylase determination. The detection of the amount of reducing substances released by the action of the amylase on the starch is by the use of the Somogyi-Nelson method of blood sugar determination

## ASCORBIC ACID

(Whole Blood)

**Reagents.** **Indophenol Reagent.**—Add approximately 10 mg. of 2,6-dichlorophenol-indophenol (sodium salt) to 100 ml. of distilled water. This need not be

weighed. After weighing one sample, subsequent samples may be roughly estimated on a knife tip. Make up fresh before using.

**Ascorbic Acid Standard (100 mg. per 100 ml.).**—One hundred milligrams of ascorbic acid plus 1 ml. of glacial acetic acid is diluted to 100 ml. with water. Make up fresh twice a week. Keep in refrigerator.

**Ascorbic Acid (1 mg. per 100 ml.).**—Wash 0.01 ml. of the 100 mg. per 100 ml. standard into 1 ml. of water. Make up just before use.

**Procedure.**—Hemolyze 1 ml. of oxalated blood with 1 ml. of distilled water. Add 2 ml. of 10% trichloroacetic acid, and centrifuge for 10 minutes. Take a 3-ml. aliquot and titrate with indophenol reagent contained in a 2-ml. buret until the pink color persists for a short duration. The standard is made up of 1 ml. of ascorbic acid standard (1 mg. per 100 ml.) and 2 ml. of 10% trichloroacetic acid. This is titrated in the same manner as the unknown. A blank consisting of 1 ml. of water and 2 ml. of 10% trichloroacetic acid is titrated.

**Calculation.**—

$$\frac{\text{Titration of unknown—blank titration}}{\text{Titration of standard—blank titration}} \times 1.33 = \text{mg. ascorbic acid/100 ml.}$$

**Notes.**—Dilute the indophenol reagent until an approximately 1-ml. titration is obtained with the standard. The indophenol solution is blue and turns pink as it mixes with the acid. The dichlorophenol-indophenol is bleached by the ascorbic acid (vitamin C). At the end point, a pale pink which persists for at least 30 seconds, is noted. The color will eventually fade due to air oxidation.

Normal blood plasma or serum contains from 0.8 to 1.5 mg. of ascorbic acid per 100 ml. Normally, red cells contain from 0.8 to 1 mg. per 100 ml. of packed cells. White cells and platelets have been shown to have levels as high as 25 mg. per 100 ml.

## BICARBONATE LEVEL OF DUODENAL SECRETIONS

The specimen is obtained by the physician after a tube has been placed into the duodenum. An alkaline specimen tells the physician that the tube is in the duodenum and not the stomach which contains acid materials. The specimen does not need to be placed under an oil seal. The determination should be performed as soon as it is received in the laboratory.

**Procedure.**—Place 1 ml. of distilled water in the cup of the Van Slyke Apparatus. Deliver 1 ml. of the duodenal secretions below the water with a pipet which is *not* graduated to the tip. Add one drop of caprylic alcohol. Proceed with the determination following the steps enumerated in the procedure for carbon dioxide using the Manometric Van Slyke Apparatus (p. 1085).

**Notes.**—Normal values: 60 to 75 milliequivalents per liter.

The bicarbonate level in duodenal secretion is determined by the application of the law of gases to the method of Van Slyke for determining CO<sub>2</sub> levels of plasma. Milliequivalents per liter of CO<sub>2</sub> are equal to milliequivalents per liter of the bicarbonate ion in the duodenal secretion.

## BILIRUBIN

(Serum)

**Reagents.** **Sulfanilic Acid Solution, 0.1%, Reagent Grade.**—Dissolve 1 g. of sulfanilic acid, reagent grade, in 15 ml. of concentrated HCl with gentle heating and dilute to 1000 ml. in a liter flask with distilled water.

**Sodium Nitrite Solution, 0.5%, Reagent Grade.**—Prepare fresh daily by dissolving 0.5 g. of sodium nitrite, reagent grade, in 100 ml. of distilled water in a 100-ml. volumetric flask.

**Diazo Reagent.**—Prepare fresh just before using by adding 0.3 ml. of 0.5% sodium nitrite to 10 ml. of 0.1% sulfanilic acid solution.

**Procedure. Direct Reacting Bilirubin.**—Place 1 ml. of serum in a large test tube. Add 9 ml. of distilled water. To each of two cuvetts, 19 by 105 mm., add 4 ml. of diluted serum. To one cuvet (blank) add 1 ml. of 1.5% HCl. Mix by inversion. To the other cuvet add 1 ml. of fresh diazo reagent. Mix by inversion. After exactly 1 minute read the per cent transmittance at 535  $m\mu$  against the reference blank which has been set at 100%  $T$  (transmittance). Obtain results from calibration curve.

**Total Bilirubin (Direct Plus Indirect Reacting Bilirubin).**—To the tubes previously used for direct reacting bilirubin determinations, proceed as follows: To all tubes add 5.0 ml. of absolute methanol; stopper and invert a few times; after 30 minutes read the per cent transmittance at 535  $m\mu$  against the blank which has been set at 100%  $T$ . Obtain results from the calibration curve.

**Calculations.**—The difference between the total bilirubin and the direct reacting bilirubin is the indirect bilirubin.

**Calibration Curve.**—Accurately weigh 20 mg. of dry bilirubin standard (phanthiel) and dilute to 100 ml. with chloroform. This is a 20 mg.% stock standard. Store in the refrigerator. Take 1 ml. of the 20 mg.% stock standard and dilute to 100 ml. with absolute methanol. This represents a 0.2 mg.% working standard. Into each of four 19- by 105-mm. cuvetts add 1 ml. diazo reagent. Into cuvet number 1 add 3 ml. of distilled water, 1 ml. of working standard, 5 ml. of absolute methanol, and allow to stand 30 minutes. This represents 0.5 mg.% bilirubin. Into cuvet number 2 add 2 ml. of distilled water, 2 ml. working standard, and 5 ml. absolute methanol. Read after 30 minutes at 535  $m\mu$  against a distilled water blank. This represents 1 mg.% bilirubin. Into cuvet number 3 add 1 ml. of distilled water, 3 ml. of working standard, and 5 ml. of absolute methanol. Read after 30 minutes at 535  $m\mu$  against a distilled water blank. This represents 1.5 mg.% bilirubin. Into cuvet number 4 add 4 ml. of working standard and 5 ml. of absolute methanol and read after 30 minutes at 535  $m\mu$  against a distilled water blank. This represents 2 mg.% bilirubin. Plot results on semilog paper.

**NOTE.**—Normal values: Direct Reacting Bilirubin 0 to 0.2 mg. per 100 ml. bilirubin. Total bilirubin 0.2 to 0.8 mg.% bilirubin.

## BROMIDE

(Serum or Spinal Fluid)

**Reagents. Stock Sodium Bromide Standard (1 ml. = 10 mg.).**—Dissolve 1 g. of c.p. sodium bromide in a 100-ml. volumetric flask with distilled water.

**Dilute Sodium Bromide Standard (1 ml. = 0.5 mg.).**—Place 10 ml. of stock standard in a 200-ml. volumetric flask and dilute to volume with a 10% trichloroacetic acid–0.6% sodium chloride mixture.

**Procedure. Serum.**—Place 18 ml. of 10% trichloroacetic acid in a large test tube and while shaking add 2 ml. of serum dropwise. Let stand 20 minutes and filter through Whatman No. 44 filter paper. Pipet 10 ml. of the filtrate into a cuvet.



Prepare a blank by placing 10 ml. of 10% trichloroacetic acid in a cuvet. Add 1 ml. of 0.5% gold chloride solution to each tube and mix. Read in the spectrophotometer at a wavelength of 520, setting the blank at 100% T.

**Spinal Fluid.**—Make a 1:5 filtrate by adding 3 ml. of spinal fluid to 12 ml. of 10% trichloroacetic acid. Proceed as described for serum bromide. Divide the value obtained by 2 to correct for the different dilution.

**Calibration Curve.**—Pipet the following amounts of the dilute standard sodium bromide solution (1 ml. = 0.5 mg.) and 10% trichloroacetic acid—0.6% sodium chloride mixture into 9 spectrophotometer tubes.

<i>Ml. of Dil. Standard Soln.</i>	<i>Ml. of 10% Trichloroacetic Acid NaCl Mixture</i>	<i>Mg. % of Sodium Bromide</i>
1	9	50
2	8	100
3	7	150
4	6	200
5	5	250
6	4	300
7	3	350
8	2	400
0	10	Blank

Add 1 ml. of 0.5% gold chloride solution to each tube and read as described in the above method. Repeat several times, average results, and plot on semilog paper.

**NOTES.**—Normal value: less than 50 mg. per 100 ml.

The therapeutic concentration is considered about 200 mg. per 100 ml. Toxic values are usually above 250 mg. per 100 ml. The ratio of blood bromide to spinal fluid bromide is about 3 to 1.

This test is based on the reaction between sodium bromide and gold chloride which yields gold bromide and produces a brown to brownish-red color. The specificity of the reaction has been questioned and some point out that chemically unrelated compounds, as well as the other halogens, may react to produce the color change. The test is sufficiently accurate for use as a diagnostic measure, but may be inadequate as an index to the progress of any given case.

## CALCIUM

(Serum, Cerebrospinal Fluid, Urine, Feces)

**Reagents.** **Standard Calcium Chloride Solution.**—Dissolve 0.2498 g. of pure calcite in a little dilute HCl in a wide evaporating dish of 50- to 100-ml. capacity, care being taken to avoid loss by spattering. Run the acid down the side of the dish, allowing the reaction to proceed slowly. Carefully evaporate the solution several times to near dryness, each time adding distilled water, and last, evaporate to near dryness, expelling the last trace of HCl. Dissolve the residue in distilled water and dilute to 1 liter. One cubic centimeter of this solution equals 0.1 mg. calcium. This standard keeps indefinitely.

**Procedure.** **Serum and Cerebrospinal Fluid.**—In a special acid-free centrifuge tube, place 2 ml. serum or cerebrospinal fluid, 2 ml. distilled water, and 1 ml. of 4% ammonium oxalate solution. (Set up in duplicate.) If 4 ml. of serum or cerebrospinal fluid are not available, test may be set up on 1 ml. serum, 3 ml.

distilled water, and 1 ml. of 4% ammonium oxalate. Mix by rotation. In a similar tube to be used for the standard, place 2 ml. of calcium chloride standard, 2 ml. of distilled water, and 1 ml. of 4% ammonium oxalate solution. Set up in duplicate and mix by rotation. Let stand one-half hour in a refrigerator or overnight at room temperature. Centrifuge (1500 to 1800 r.p.m.) for 10 minutes. Invert the tubes and drain off the supernatant fluid. Mix packed precipitate by tapping tube. Add slowly 3 to 4 ml. of 2% ammonium hydroxide solution. Mix thoroughly by rotation. DO NOT invert. Centrifuge 7 minutes at 1500 to 1800 r.p.m. Decant, mix precipitate, and wash once more with 2% ammonium hydroxide solution. After the second washing, decant, mix precipitate, and add 2 ml. of 1 N  $\text{H}_2\text{SO}_4$ . Boil 1 minute to dissolve precipitate and transfer to 75°C. water bath and titrate immediately. Titrate with 0.01 N potassium permanganate solution to a faint pink. Titrate the two standard tubes first. Maximum allowable variation in duplicate tubes is 0.06 ml.

Calculations.—

$$\frac{\text{Ml. KMnO}_4 \text{ used in titration (patient)}}{\text{Ml. KMnO}_4 \text{ used in titration (standard)}} \times 10 = \text{mg. per 100 ml. of calcium.}$$

Feces.—Ignite the complete specimen in a covered casserole or other container. Heat until the sample is completely reduced to a fluffy white or gray ash. When the ashing process is completed, cool and carefully add the minimum amount of concentrated hydrochloric acid required to dissolve the ash. Keep the dish as nearly covered as possible while dissolving the ash to avoid loss by spattering. Without filtering, transfer the entire solution to a 100-ml. volumetric flask and dilute to the mark with distilled water. (If patient is on a normal calcium intake diet, use a 0.5-ml. aliquot.) Proceed as for the serum determination using a 1 ml. aliquot.

Calculations.—We are dealing with a quantity of calcium expressed in *mass* units rather than in *concentration* units, and this must be taken into account in the calculations. By definition, any concentration unit is converted into a mass unit when multiplied by the volume taken. Thus if the standard solution contained 0.1 mg. per ml. and we took 2 ml., we actually had 0.2 mg. of calcium. So for stools use the following equation:

$$\text{Mg. Ca/24 hours} = \frac{\text{vol. KMnO}_4 \text{ test}}{\text{vol. KMnO}_4 \text{ std.}} \times \text{conc. std.} \times \text{vol. std.} \times \frac{100}{\text{aliquot}}$$

where the concentration of the standard is in mg.%, the volumes are in milliliters, and the last factor corrects for the aliquot of the 100-ml. solution of stool ash.

Urines.—Measure the total urine volume, including any precipitate which may be present. Thoroughly mix the specimen and adjust its reaction just to the acid side of litmus by *dropwise* addition of concentrated hydrochloric acid or ammonium hydroxide, depending on the original reaction. If this is properly done, the major part of any sediment will rapidly dissolve.

Take a 1-ml. aliquot of the mixed sample and place it in a 50-ml. Kjeldahl flask along with 0.5 ml. of concentrated nitric acid. Add a few glass beads. Large beads should be avoided as they interfere with centrifugal packing of the precipitated calcium oxalate. Slowly bring to boiling and continue to drive off water until the volume in the flask is almost dry. Cool the flask slightly and add

slowly, down the side, about 1 ml. of 30% hydrogen peroxide (Superoxol or similar quality). When the vigorous reaction has ceased, continue heating the flask to dryness. (*Avoid undue baking of the residue; just remove obvious liquid.*) The sample will appear to ignite spontaneously just before reaching the proper state of dryness. This is normal behavior. Allow the flask to cool and take up the residue in about 3 ml. of distilled water. If the solution is colored by oxides of nitrogen, repeat the treatment with hydrogen peroxide and again take to dryness. Finally dissolve the residue in a small amount of distilled water. Without filtering, transfer the contents of the flask to a 15-ml. centrifuge tube; rinse the flask with 2 ml. of water and add this to the tube also. Total volume will be 5 ml. Proceed as with serum determination.

Calculations.—For urines use the following equation:

$$\text{Mg. Ca/24 hours} = \frac{\text{vol. KMnO}_4 \text{ test}}{\text{vol. KMnO}_4 \text{ std.}} \times \text{conc. std.} \times \text{vol. std.} \times \frac{\text{total vol.}}{\text{aliquot taken}}$$

where total volume refers to the urine sample and the aliquot refers to the 1 ml. originally taken for analysis. The other symbols have the same significance as in the calculations above for fecal calcium.

NOTES.—Both urine and feces contain iron and magnesium which also give insoluble oxalates. Careful attention to reaction of the solution will avoid coprecipitation of these ions. The presence of organic material which easily reduces permanganate makes necessary the pretreatment outlined. Use *unscratched* centrifuge tubes, acid-washed.

Normal values: 9 to 11.5 mg. per 100 ml. (serum); 0.1 to 0.3 g. per 24 hr. (urine).

## CARBON DIOXIDE CONTENT

(Serum and Plasma by the Van Slyke-Neill Manometric Apparatus)

**Procedure.**—Preceding each analysis, the apparatus is cleaned by introducing 10 ml. of lactic acid solution and 10 ml. of distilled water, shaking for 15 or 20 seconds in the evacuated chamber, and ejecting the extracted gas and solution. The chamber is rinsed once with water, ejecting a few drops of mercury following the water. Remove excess water from the cup with an aspirator or medicine dropper and fill the stopcock channel with mercury by opening the stopcock, raising bulb to the upper level, and closing the stopcock.

Place three drops of caprylic alcohol in the cup and admit enough to fill the stopcock channel (leveling bulb should be in lower position). Add 3.0 ml. of 0.1 *N* lactic acid to the cup. Add exactly 1 ml. of serum or plasma to the cup holding the pipet tip close to the bottom so that the serum is layered beneath the lactic acid. The serum and 2.5 ml. of the lactic acid are admitted into the reaction chamber (1 ml. of the lactic acid and some caprylic alcohol are left in the cup). Add mercury to the cup, and admit enough to seal the stopcock channel. Lower the leveling bulb below the lower support and draw the mercury meniscus to the 50-ml. mark just below the reaction chamber. Close the stopcock leading to the bulb and shake for 3 minutes. Open the stopcock leading to the bulb and rapidly raise the *solution* meniscus to the 2-ml. mark just above the reaction chamber. Quickly read initial gas pressure ( $P_1$ ) on the manometer.

Add 2 ml. of 10% NaOH solution to the cup and slowly admit 1 ml. into the reaction chamber. Seal the stopcock with mercury and remove excess alkali and mercury from the cup by aspiration. Raise and lower the bulb three times to

ensure complete mixing of the aqueous solution and absorption of  $\text{CO}_2$  by the alkali. Bring the solution meniscus to the 2-ml. mark and read  $P_2$  on the manometer. Record the temperature of the water jacket. Expel the solution through the side arm and clean chamber as noted above.

**Blank.**—Use the carbon dioxide content method described above with 3.5 ml. of lactic acid. This value represents the amount of carbon dioxide in the reagent. The blank is usually 1 mm. to 4 mm.

**Calculations.**—Since  $P_1$  equals millimeters of the initial gas pressure and  $P_2$  equals millimeters of pressure due to all gases except carbon dioxide, then  $P_1 - P_2$  equals millimeters of carbon dioxide pressure. Subtract the blank from this value and multiply the resulting pressure by the appropriate factor. The factor varies with the temperature and the factors for the method described here are

TABLE 30-1. FACTORS FOR CARBON DIOXIDE CONTENT METHOD

Temperature, °C.	Factor	Temperature, °C.	Factor
15	0.1231	25	0.1167
16	0.1224	26	0.1161
17	0.1217	27	0.1156
18	0.1211	28	0.1151
19	0.1204	29	0.1145
20	0.1198	30	0.1140
21	0.1192	31	0.1135
22	0.1185	32	0.1130
23	0.1179	33	0.1125
24	0.1173		

listed in Table 30-1. A complete list of factors is available in the literature. The formula for the calculation is:

$$(P_1 - P_2) - \text{blank} \times \text{factor} = \text{milliequivalents per liter of } \text{CO}_2$$

**NOTES.**—Normal values: 25 to 30 milliequivalents per liter.

The sample to be analyzed may be handled in two ways. Care must be taken in order that carbon dioxide does not escape before the performance of the test. The blood, therefore, may be either collected under oil or by means of the heparinized vacutainer tube. In our experience the vacutainer is perfectly adequate and is much easier to handle.

## TOTAL CATECHOLAMINES

(Urine)

**Reagents.** Activated Alumina, Alcoa, grade F-20, 60 to 200 mesh.

**Acetate Buffer.**—Add 6 ml. of 10 *N* sodium hydroxide to 100 ml. of saturated sodium acetate solution.

**Ascorbic acid-sodium hydroxide reagent,** prepared immediately before use by adding 0.5 ml. of ascorbic acid, 2% (wt./vol.) to 4.5 ml. of sodium hydroxide, 20% (wt./vol.).

**Stock Standard Noradrenalin.**—Dissolve 20.1 mg. of levarterenol bitartrate, USP, in 100 ml. of 0.1 *N* hydrochloric acid; 1 ml. contains 100  $\mu$ g. of noradrenalin. This remains stable for at least six months in the refrigerator.

**Working Noradrenalin Standard.**—Dilute 0.5 ml. of stock standard solution to 50 ml. of distilled water; 0.5 ml. contains 0.5  $\mu$ g. of noradrenalin. This solution should be freshly prepared just before needed.

**Procedure. Collection of Samples.**—Urine specimens are conveniently collected in a 1-ounce polyethylene bottle containing 0.2 g. of the following preservative mixture: 4 g. sodium metabisulfite plus 2 g. sodium fluoride. The urine samples are preserved in this way at room temperature for a period up to one week.

**Determination.**—To an approximately 20-ml. sample of urine in 125-ml. Erlenmeyer flask add 6 *N* sulfuric acid to pH 2 (pH test paper). Cover the mouth of the flask with a small funnel, heat in a boiling water bath for 20 minutes, then cool in running tap water. Add 14% sodium carbonate to pH 8.5, using narrow range pH paper. Centrifuge. Chromatograph to clear supernatant without delay.

The chromatographic tube to be used is 8 by 130 mm., and it is sealed to a reservoir 25 by 65 mm. Add the alumina, suspended in water, to the tube until the column 4 cm. in height is obtained. Wash the column with 5 ml. of 0.2 *M* sodium acetate trihydrate solution, and add 10 ml. of urine. Wash the column first with 20 ml. of 0.2 *M* sodium acetate, and then with 5 ml. of distilled water. Elute the catecholamines with 0.2 *M* acetic acid; collect 20 ml. of eluate.

The fluometric procedure which follows is used for the determination of total catecholamines. Transfer 4.0-ml. aliquots of urine eluate to each of three tubes: (a) blank, (b) sample, (c) sample plus standard. To tubes (a) and (b) add 0.5 ml. of distilled water and to tube (c) add 0.5 ml. of working noradrenalin standard. Add to each tube 1.0 ml. of acetate buffer; resulting pH should be between 6.0 and 6.5 (narrow range pH paper). Add 0.1 ml. of 0.25% (wt./vol.) potassium ferricyanide reagent to each tube and allow to stand 2 minutes. To tube (a) (blank) add 1.0 ml. of 20% sodium hydroxide (wt./vol.); allow to stand 20 minutes, centrifuge and determine fluorescence as described below. To tubes (b) and (c), add 1.0 ml. of ascorbic acid-sodium hydroxide reagent, centrifuge and read the fluorescence immediately in a photofluorometer using Corning filters, 5970 (primary) and 3387 (secondary).

**Calculation.**—Subtract the "blank" fluorescence from the "sample" fluorescence. This gives the "corrected sample fluorescence." Subtract the "sample" fluorescence from the fluorescence of the "sample plus standard." This gives the "standard" fluorescence.

$$\frac{\text{Corrected sample fluorescence}}{\text{Standard fluorescence}} \times 25$$

=  $\mu$ g. catecholamines/100 ml. calculated as noradrenalin

**NOTE.**—Normal individuals excrete less than 200  $\mu$ g. of catecholamines per 24 hours. In the presence of pheochromocytoma, excretion of catecholamines is markedly increased.

## CHLORIDES

(Serum, Spinal Fluid, Urine)

**Reagents. Mercuric Nitrate Solution.**—Dissolve 5 g. of mercuric nitrate (c.p.) in 500 ml. of distilled water which has been acidulated with 2.5 ml. of concentrated nitric acid. Dilute to 1 liter in a volumetric flask and mix. The solution is stable. (Accuracy in weighing the mercuric nitrate is important.)

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**Indicator Solution.**—Dissolve 100 mg. of *s*-diphenylcarbazon in 100 ml. of 95% ethyl alcohol. Store in the refrigerator in a brown bottle. Prepare a fresh solution monthly.

**Chloride Standard (100 milliequivalents per liter).**—Dry 6 g. of c.p. sodium chloride at 110° C. for 1 hour and cool to room temperature in a desiccator. Accurately weigh 5.845 g. and dissolve in distilled water. Dilute to 1 liter in a volumetric flask and mix. The solution is stable indefinitely.

**Procedure.**—To 5 ml. of distilled water in a 50-ml. Erlenmeyer flask, add 0.5 ml. of serum, urine, or spinal fluid. (For urine, measure the volume of a 24-hour specimen.) Add 0.5 ml. of a 100 milliequivalent per liter standard chloride solution to 5 ml. of distilled water in a similar flask. To each flask add four drops (0.06 ml.) of *s*-diphenylcarbazon indicator. If, on the addition of the indicator to the unknown, a pink color develops, add approximately 1 *N* nitric acid dropwise (0.02 ml.) until the color just disappears. Avoid adding an excess of nitric acid. The *s*-diphenylcarbazon is colorless at pH 6, faint pink at pH 7, and salmon-pink at pH 8. The most desirable pH is 4.5 to 6.6 at the beginning of the titration. Titrate the samples by adding mercuric nitrate solution from a 5-ml. buret calibrated in 0.02-ml. divisions. The end-point color is violet-blue.

**NOTES.**—Blood specimens for chlorides should be drawn without stasis and hemolysis. The serum must be separated promptly from the cells to prevent cell chlorides from entering the serum. (The red cell chloride content is about one-half that of serum.) The test should be run as soon as possible after collection. Abnormal amounts of bromine present in the specimen will elevate the results of the test since mercuric nitrate does not differentiate between chloride and bromide. It is not necessary to use exactly 5 ml. of water as a diluent in step No. 1, but it is preferable to use approximately this amount. Too little or too much water makes the end point difficult to read.

**Calculations.**—Serum and spinal fluid (report in milliequivalents per liter):

$$100 \times \frac{\text{vol. Hg(NO}_3)_2 \text{ unknown}}{\text{vol. Hg(NO}_3)_2 \text{ standard}} = \text{milliequivalents/liter}$$

Urine (report in grams per 24 hours):

$$100 \times \frac{\text{vol. Hg(NO}_3)_2 \text{ unknown}}{\text{vol. Hg(NO}_3)_2 \text{ standard}} \times 0.035 \times \text{no. liters in spec.} = \text{g./24 hours}$$

**Normal values**    96 to 105 milliequivalents per liter (serum)  
                          118 to 130 milliequivalents per liter (spinal fluid)  
                          0.4 to 0.6 g. per 100 ml., or 6 to 10 g./per 24 hours (urine)

### CHOLESTEROL, FREE AND TOTAL (Serum)

**Reagents. Digitonin Solution.**—Dissolve 1 g. of digitonin in 50 ml. ethanol. Dilute to the mark in a 100-ml. volumetric flask with distilled water.

**Iron Stock Solution.**—Dissolve 2.5 g. of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 25 ml. of glacial acetic acid. Preserve in the freezing compartment of the refrigerator and thaw when needed. No precipitate forms in the thawed solution.

**Color Reagent.**—Pipet 1.0 ml. of the stock iron solution into a 100-ml. volumetric flask and dilute to the mark with sulfuric acid (c.p.) with continuous swirling. Discard when any precipitate becomes evident.

**Cholesterol Stock Standard Solution.**—Dissolve 100 mg. of pure cholesterol in glacial acetic acid and dilute to the mark in a 100-ml. volumetric flask with mixing.

**Procedure.**—Place about 10 ml. of a 50:50 alcohol-acetone mixture into a 25-ml. volumetric flask. Add 1.0 ml. of serum to the mixture with vigorous swirling. Bring mixture to a boil in a hot-water bath. Mix constantly while heating to avoid bumping. Cool and dilute to the 25-ml. mark with the alcohol-acetone mixture. Filter through Whatman No. 41-H filter paper, keeping funnel top covered to prevent evaporation. Pipet 2.5-ml. aliquots of the filtrate into a 30-ml. test tube (for total cholesterol) and into a 15-ml. conical centrifuge tube (for free cholesterol). Place both tubes in a hot-water bath. *Caution:* gradually increase heat for free cholesterol. Evaporate the contents of the test tube to dryness and the centrifuge tube to 0.5 to 1.0 ml.

**Total Cholesterol.**—Add 3 ml. of glacial acetic acid to the test tube containing the dry residue. Warm 30 seconds in a water bath until the residue is resuspended.

**Free Cholesterol.**—Add 1 ml. of a 1% digitonin solution to the partially evaporated contents of the centrifuge tube. Mix well by tapping tube. Allow to stand for 10 minutes. Centrifuge for 10 minutes at 3500 r.p.m. Decant the supernatant fluid and allow the inverted tube to drain for several minutes on absorbent paper. Blow 4.0 ml. of acetone into the tube to disperse the precipitate. Mix thoroughly. Centrifuge for 10 minutes, decant and drain (as above). Add 3 ml. of glacial acetic acid. Warm a few seconds in the water bath, if necessary, to dissolve the precipitate.

Add 2 ml. of the color reagent to all tubes. Mix thoroughly. Cool for 5 minutes. Read the absorbance in the spectrophotometer at 620  $m\mu$  using a 10- by 75-mm. cuvet. Make readings against a reagent blank consisting of 3 ml. of glacial acetic acid and 2 ml. of color reagent.

All glassware used for this test must be water free. Red blood cells contain smaller concentrations of free cholesterol; therefore, hemolyzed specimens are unsatisfactory. The serum contains a potent cholesterol esterase enzyme which rapidly esterifies free cholesterol when blood is allowed to remain at room temperature. If the test cannot be performed soon after the specimen is collected, the serum should be separated and frozen. The results may be erroneously high in the presence of traces of bromide. This interference can be removed by shaking the serum sample for about 5 minutes with 25 to 50 mg. per ml. of solid silver iodate and then centrifuging briefly. The clear supernatant serum is then analyzed as outlined.

**Calculations.**—1. Values for total cholesterol (mg. per 100 ml.) are obtained from a calibration curve.

2. Values for free cholesterol (mg.%) are obtained from a calibration curve.

3. Cholesterol esters (mg.%) = total cholesterol (mg.%)—free cholesterol (mg.%).

**Calibration Curve.**—Pipet 0.0, 0.1, 0.2, and 0.3 ml. of the stock cholesterol standard solution into a 30-ml. test tube. Add glacial acetic acid to each tube to make a final volume of 3 ml. Add 2 ml. of color reagent to each tube, mix thoroughly, and allow to cool. Measure the absorbance of each tube at 620  $m\mu$  using a 10- by 75-mm. cuvet. Plot the readings against their corresponding dilutions on graph paper.

**NOTES.**—Normal values: Total cholesterol—150 to 250 mg. per 100 ml. Cholesterol esters—approximately 65 to 75% of total. These are average figures. There may be variations among normal individuals over a wide range which may extend from 110 to 350 mg. per 100 ml. for total cholesterol. Of this, about one-third is present as free cholesterol, and the balance is in esterified form. Since not only age, but the sex and the diet (high animal fat) affect the serum cholesterol level, the establishment of a standard normal range is difficult.

## COPPER

(Serum and Urine)

**Reagents. Color Reagents.**—Weigh out 100 mg. of bathocuproine. (G. F. Smith Chemical Company, Columbus, Ohio; c.p. grade.) Add 0.5 ml. of iron-free chlorosulfonic acid and heat over the flame of a microburner for 30 seconds. Cool, carefully add 10.0 ml. of contaminate-free distilled water to the container and warm in a water bath with stirring to dissolve all solid material. Dilute 3.0 ml. of the reagent to 100 ml. with 45% sodium acetate solution, filter off any insoluble material and store in a brown glass-stoppered bottle. The reagent appears to be stable for several months stored in brown glass-stoppered bottles.

**Copper Stock Standard.**—Weigh out 100 mg. of analytical grade copper shot or purified copper powder, dissolve in sulfuric acid solution, and dilute to 1 liter.

**Copper Working Standards.**—Dilute 0.0, 1.0, 2.0, 3.0, and 4.0 ml. of the copper stock standard to 100 ml. with distilled water. These correspond to concentrations of 0 to 400 mg. per 100 ml.

**Procedure.**—Pipet 1.0-ml. sample of serum or urine into a clean, dry, glass-stoppered centrifuge tube. Prepare blank for the analyses by substituting 1.0 ml. of contaminate-free distilled water for the serum, 0.5 ml. of contaminate free distilled water for the trichloroacetic acid, and proceed as below for serums. Prepare standards by pipetting 1.0 ml. of each of the copper working standard into a tube and treat as described for the blank samples.

Add 1.0 ml. of 1 N HCl to a tube, mix and heat for 5 minutes in a near boiling water bath. Cool, and add 0.5 ml. of 10% trichloroacetic acid and mix thoroughly with a clean glass rod or by vigorously shaking the stoppered container. Centrifuge at 3500 to 4000 r.p.m. for 15 minutes. Pipet 1 ml. of the clear supernatant solution into a clean cuvet (10 by 75 mm.). Add a small spatula tipful (approximately 10 mg.) of solid ascorbic acid to the cuvet, and mix well. (The amount of ascorbic acid added is not critical.) Add 0.2 ml. of the bathocuproine color reagents, and mix well. Read the sample against its appropriately prepared blank at 485 mμ.

**Calculations.**—

$$\text{Copper, } \mu\text{g. per 100 ml.} = \frac{\text{absorbance of unknown}}{\text{absorbance of standard}} \times \text{conc. of standard}$$

**NOTES.**—Because the procedure is so delicate and the amounts of ions being dealt with are measured in micrograms, it is necessary that all glassware being used in the procedure be extremely clean. Care must be taken not to overheat the serum and thus coagulate the protein.

Normal values: 150 to 200 μg. per 100 ml. of serum for copper. The usual analytical procedures for the assay of serum copper and iron are quite difficult. By the use of sulfonated phenanthrolines one is able to determine the serum copper and iron with relative ease. The phenanthrolines form complexes with copper and iron. These complexing agents are 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline) for iron, and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine) for copper. The sulfonation of bathophenanthroline with chlorosulfonic acid makes these colored complexes water soluble.



## CREATINE AND CREATININE

(Serum, Plasma, Urine)

**Reagents.** Alkaline Picrate.—Mix 8 parts of picric acid solution (1%) to 2 of 10% sodium hydroxide and allow to stand for 10 minutes before use. Prepare daily.

**Creatinine Stock Standard (1 mg. per ml.).**—One gram of creatinine dried at 80°C. is made up to 1 liter with 0.1 *N* HCl (8.5 ml. concentrated HCl up to 1 liter). Cover this solution with toluene and keep in the refrigerator.

**Creatinine Dilute Standard (10  $\mu$ g. per ml.).**—Dilute 1 ml. of stock standard to 100 ml. with water. This dilute standard is good for one day only.

**Creatine Stock Standard (Equivalent to 1 mg. per ml. of Creatinine).**—Creatine is recrystallized from water and dried at 80°C. Transfer to a vacuum desiccator and dry overnight. Place 1.16 g. of creatine in a liter flask and make to the mark with 0.1 *N* HCl. Cover with toluene and keep in the refrigerator. Creatine occurs as the monohydrate. It should be analyzed by the Kjeldahl method for nitrogen content to assure the anhydrous state.

**Creatine Dilute Standard (Equivalent to 10  $\mu$ g. of Creatinine per ml.).**—Dilute the creatine stock standard 1:100. Keep under toluene and in the refrigerator. Make up daily.

**Tungstic Acid.**—Mix equal parts of 0.15 *N* sulfuric and 2.2% (wt./vol.) sodium tungstate solution.

**Procedure for Urine (Preformed Creatinine).**—Record the volume of a 24-hour sample. To a test tube with a mark at 10 ml., add 0.1 ml. of urine. Now add 4 ml. of picric acid solution (1%) followed by 1.0 ml. of 10% NaOH. Mix and let stand for 10 minutes. Dilute to the 10-ml. mark and read after 15 minutes with the 52 filter in the Klett-Summerson colorimeter or at 490  $m\mu$  in the Beckman spectrophotometer. The blank comprises 4 ml. of 1% picric acid with 1.0 ml. of 10% NaOH made up to 10 ml. Read the concentration of creatinine from the standard curve (see below). Check the curve by adding 0.1 ml. of the creatinine stock standard (1 mg. per ml.) and treating as for urine.

**Procedure for Urine (Creatine).**—This test must be run alongside of the creatinine assay. To 0.1 ml. of urine add 4 ml. of 1% picric acid. Cover the tube with tin foil and place in the steam autoclave at 120°C. for 30 minutes. Cool under the running tap after removal from the autoclave. Add 1.0 ml. of 10% NaOH and mix. Allow to stand 10 minutes, dilute to the 10-ml. mark, and read as for creatinine. Treat the creatine standard as for the unknown, using 0.1 ml. of creatine standard instead of the urine. This assay determines total creatinine; and therefore, read the concentration as creatinine from the standard creatinine chart for urine.

**Calculations.**—

Total creatinine (after heating) — preformed creatinine = creatinine due to creatine

Creatinine due to creatine  $\times 1.16$  = creatine concentration

**Procedure for Plasma or Serum (Preformed Creatinine).**—To 1.0 ml. of cell free and unhemolyzed serum, add 7.0 ml. of tungstic acid. Mix and centrifuge for 10 minutes at 2000 r.p.m. Decant the supernatant into another tube. Use a 3-ml. aliquot for creatinine and a 3-ml. aliquot for creatine.

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To a 3-ml. aliquot add 0.8 ml. of 1% picric acid solution and 0.2 ml. of 10% NaOH. Allow to stand for 10 minutes and read before 15 minutes have elapsed. Read the creatinine concentration directly from the calibration chart made for serum. The blank uses 1 ml. of water treated as for serum, adding 7 ml. tungstic acid, taking a 3 ml. aliquot, etc. For the standard, use 1 ml. of the dilute creatinine standard (10  $\mu$ g. per ml.) and treat as for serum.

**Procedure for Plasma or Serum Creatinine.**—To a 3-ml. aliquot of the centrifugate of serum (see procedure above for plasma or serum creatinine) add 0.8 ml. of 1% picric acid. Place in a steam autoclave for 30 minutes at 120°C. Cool under the tap, add 0.2 ml. of 10% NaOH and mix. Allow the color to develop for 10 minutes and read before 15 minutes. For the standard, add 1 ml. of the dilute creatine standard (10  $\mu$ g. per ml.) to 7 ml. of tungstic acid, take a 3-ml. aliquot, add 0.8 ml. of picric acid, and heat as for the unknown. For the blank treat 1 ml. of water, as for the serum. Read the concentrations from the standard creatinine curve for serum. The standard should check the standard curve.

### Calculations.—

Total creatinine (after heating) — preformed creatine = creatinine due to creatine

Creatinine due to creatine  $\times 1.16$  = creatine concentration

**Standard Curves. Creatinine for Urine.**—To a series of 8 tubes marked at 10 ml. add 0.5 ml. of water (blank), 0.1 ml. of creatinine stock standard (100 mg. per 100 ml.); 0.1 ml. of stock standard diluted 1:1 with water (50 mg. per 100 ml.); 0.1 ml. of stock standard diluted 1:3 with water (25 mg. per 100 ml.); 0.2 ml. of stock standard (200 mg. per 100 ml.); 0.3 ml. of stock standard (300 mg. per 100 ml.); 0.4 ml. of stock standard (400 mg. per 100 ml.); and 0.5 ml. of stock standard (500 mg. per 100 ml.). Now add water to those solutions in which the volume is less than 0.5 ml., so that all volumes are 0.5 ml. Add 5 ml. of alkaline picrate to each tube, mix, and let stand for 10 minutes. Dilute to 10 ml. and read against the blank before 15 minutes have elapsed. Draw the curve, plotting concentration against optical density reading. This curve will read directly in urine concentration.

**Creatinine for Serum or Plasma.**—Make up a series of solutions containing in 3-ml. volume 2.5, 5.0, 10, 15, 20, 30, and 50  $\mu$ g. of creatinine. These solutions are made from the 10  $\mu$ g. per ml. solution except for the solution containing 50  $\mu$ g., which is made by using 0.05 ml. of the stock standard (1 mg. per ml.). To one tube (blank) add 3 ml. of water. Add 1 ml. of alkaline picrate to each, and read after 10 minutes but before 15 minutes have elapsed. Since the 3-ml. aliquot taken in analyzing for the unknown contains  $\frac{3}{8}$  ml. of serum, then if, for example, the reading is equivalent to the 10  $\mu$ g. point on the standard curve,

$$10 \times \frac{100}{\frac{3}{8}} = 2667 \mu\text{g. creatinine per 100 ml. of serum} = 2.667 \text{ mg. per 100 ml. of serum}$$

The formula then becomes,

$$\mu\text{g. taken} \times 0.2667 = \text{mg. per 100 ml. creatinine}$$

Thus, 2.5  $\mu$ g. = 0.67; 5  $\mu$ g. = 1.33; 15  $\mu$ g. = 4.0; 20  $\mu$ g. = 5.33; 30  $\mu$ g. = 8.0; and 50  $\mu$ g. = 13.3 mg. per 100 ml. of serum. The curve is plotted to read directly in milligrams per 100 ml. of serum.

**NOTES.**—Picric acid forms a colored complex in alkaline solution with creatinine, with maximum absorbance at 490 m $\mu$ . The intensity of the color developed depends upon the temperature, concentration of alkali, and picric acid and the time. Thus, if room temperature rises above 25°C. or drops below 20°C., it is best to place the tubes in a constant temperature bath or a large volume of water maintained at 20° to 25°C. When creatinine estimation alone is performed, the alkali and picric acid are mixed before addition (alkaline picrate).

The molecular weight of creatine is 131 and the molecular weight of creatinine is 113. The ratio 131/113 = 1.16 is the factor required to convert creatinine values to creatine values. Creatine as first crystallized is a monohydrate. If used as such, its creatine content should be assayed by its Kjeldahl nitrogen content.

Creatinine is excreted in the urine of the normal adult at the rate of 1 to 1.7 g. daily. More specifically, 20 to 26 mg. per kilogram of body weight in males and 14 to 22 mg. per kilogram of body weight in females is excreted in 24 hours. Creatine excretion is low in normal urine and is of the order of  $\frac{1}{10}$  (25 to 200 mg.), the creatinine excretion in the normal adult when done by the Jaffe reaction. In infants of less than one year, 10 to 14 mg. per kilogram of body weight of creatine is excreted. Whole blood levels for creatine range from 3 to 7 mg. per 100 ml. and 1 to 2 mg. per 100 ml. for serum. For creatinine whole blood levels range from 1 to 2 mg. per 100 ml. and serum levels from 1 to 1.5 mg. per 100 ml.

## FIBRINOGEN

(Whole Blood)

**Reagents.** Parfentjev Ammonium Sulfate Reagent.—Dilute 133.33 g.  $(\text{NH}_4)_2\text{SO}_4$ , 10.0 g. NaCl, 0.025 g. Merthiolate to 1 liter with distilled water. Adjust to pH 7.0 with 10 M NaOH.

**Procedure.**—Collect 5 ml. of the patient's blood in a Wassermann tube containing 0.5 ml. of 4% sodium citrate dihydrate. Centrifuge specimen at 2500 r.p.m. for 10 minutes. Form the "blank" and "test" as follows: "blank"—1.0 ml. plasma plus 9.0 ml. normal saline; "test"—1.0 ml. plasma plus 9.0 ml. of the Parfentjev ammonium sulfate reagent.

In exactly 3 minutes read the blanks and the test in the spectrophotometer at wavelength 510 m $\mu$ , using a cuvet 19 by 75 mm. Read absorbance. If coagulation has occurred, the sample is given a vigorous shake just before the reading is taken.

**Calculations.**—

$$\text{Grams per 100 ml. fibrinogen} = \frac{\text{absorbance} + 0.019}{0.509}$$

**NOTE.**—Normal value: 0.113 to 0.380 g. per 100 ml.

## GASTRIC ACIDITY

(Gastric Contents)

**Reagents.** Töpfer's Reagent.—Place 1 g. of *p*-dimethylaminoazobenzene in a 100-ml. volumetric flask and dilute to the mark with 95% ethyl alcohol.

**Procedure.**—Centrifuge gastric contents. Consider specimens composed entirely of mucus or saliva unsatisfactory for determination. Test the pH of each original specimen. If free acid is present the pH will be below 4.5. Place 1 ml. in a 50-ml. Erlenmeyer flask and add approximately 10 ml. of distilled water and mix. Add two drops of Töpfer's reagent. If free acid is present, the specimen in the flask will turn red. If it turns yellow, no free acid is present. Add two drops of phenolphthalein. Titrate the free acid, if present, from red to yellow, and the total acid from yellow to red, with 0.1 N NaOH using a buret. Record the amount of NaOH for each indicator change.

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## Calculations.—

$$\text{Free acid: ml. of } 0.1 \text{ } N \text{ NaOH} \times \frac{100}{\text{ml. gastric contents used}} \\ = \text{free HCl per 100 ml. gastric contents}$$

$$\text{Total acid: ml. of } 0.1 \text{ } N \text{ NaOH} \times \frac{100}{\text{ml. gastric contents used}} \\ = \text{total acid per 100 ml. gastric juice}$$

NOTES.—Normal values for free HCl in healthy, well-nourished adults:

Males:	100 degrees (at 25 years)
	67 degrees (at 65 years)
Females:	82 degrees (at 25 years)
	67 degrees (at 65 years)

(Values expressed in degrees are equivalent to the number of milliliters of 0.1 *N* sodium hydroxide required for the neutralization of 100 ml. of gastric contents.)

## GLUCOSE

(Whole Blood, Serum, Spinal Fluid)

**Reagents.** **Glucose Stock Standard Solution (100 mg. %).**—Accurately weigh 1.000 g. of highest purity glucose on the analytical balance. Dissolve in 50 ml. of 0.25% benzoic acid. Dilute to 1 liter with 0.25% benzoic acid. Store in the refrigerator. Stability is indefinite.

**Copper Reagent.**—Dissolve 12 g. of sodium carbonate (anhydrous) and 6 g. of Rochelle salt (sodium potassium tartrate) in approximately 100 ml. of distilled water. Add 40 ml. of 5% copper sulfate pentahydrate and mix well. Add 8 g. of sodium bicarbonate and stir until dissolved. Dissolve 90 g. of anhydrous sodium sulfate in 250 ml. of hot water. Cool and add to the copper sulfate mixture. Mix well and dilute to 500 ml. with distilled water.

**Arsenomolybdate Color Reagent.**—Dissolve 50 g. of ammonium molybdate in 900 ml. of distilled water. Add 42 ml. of concentrated sulfuric acid, and mix. Dissolve 6 g. of pulverized sodium arsenate ( $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ) in 50 ml. of distilled water and add to the mixture. Mix well and place in an incubator at 37°C. for 24 to 48 hours. Store in a brown bottle.

**Procedure.**—Prepare a protein-free filtrate in a 50-ml. Erlenmeyer flask as follows:

- 15 ml. of distilled water.
- 1 ml. of oxalated blood, serum, or spinal fluid.
- 2 ml. of 5% copper sulfate.
- Mix well and allow to stand for 1 minute.
- Add, with continuous shaking, 2 ml. of 10% sodium tungstate.
- Mix well and allow to stand 1 minute.
- Filter through a dry No. 40 Whatman filter paper, or centrifuge for 15 minutes at 1800 r.p.m.

This filtrate is a 1:20 dilution of the original specimen.

Use this filtrate for glucose determinations only. Nonglucose reducing materials present in the specimen are precipitated, leaving "true sugar," only, in the filtrate.

About one-half of the precipitated reducing substance consists of nitrogenous constituents of the blood including creatine, creatinine, uric acid, urea nitrogen, and non-protein nitrogen. Breakdown of glucose takes place very rapidly in blood or spinal fluid. In blood samples, enzymes glycolyze the sugar and in infected spinal fluid bacteria destroy sugar. Greater accuracy in the test may be obtained by observing the following steps:

a. If clotted blood is used, remove the serum as soon as possible after the specimen is collected.

b. Collect whole blood in a container which includes sodium fluoride (an enzyme inhibitor). Even in the presence of fluoride, blood samples may lose as much as 10% of their sugar over a period of a few hours.

c. Make filtrates of the specimens as soon as possible after acquisition. Filtrates remain stable indefinitely. Whole blood (without fluoride) or spinal fluid may lose 10% of its glucose content per hour at room temperature.

d. If analysis is unavoidably delayed, refrigeration of the specimen may retard glycolysis for several hours.

Transfer 2 ml. of protein-free filtrate to a Folin blood sugar tube. Into a second Folin blood sugar tube place 2 ml. of distilled water. This is the reference blank. To each tube add 1 ml. of copper reagent. Mix well. Immediately place the tubes in a boiling water bath for 10 minutes. Cool without shaking in a cold-water bath for 2 minutes. To each tube add 1 ml. of arsenomolybdate color reagent. Mix well and allow to stand for 2 minutes. Dilute to 25 ml. with distilled water. Insert clean rubber stoppers in the tubes and mix by inverting the tubes three times, allowing the bulbs in the bottom of the tubes to empty each time. Read the per cent transmittance (%  $T$ ) of the unknown against the reference blank set at 100%  $T$  at 480  $m\mu$  in the spectrophotometer. Use 19- by 105-mm. cuvetts. Obtain glucose values in mg. per 100 ml. from the calibration chart.

**Calibration Curve.**—Into each of five 100-ml. volumetric flasks add, respectively, 2, 4, 6, 8, and 10 ml. of stock standard glucose solution (1 mg. per ml.). Dilute each to 100 ml. with distilled water. Two milliliters of each of these dilute standards are equivalent respectively to 40, 80, 120, 160, and 200 mg.% of blood sugar. Add 2 ml. of each standard to separate Folin sugar tubes and proceed as above. Plot the readings of the dilutions against their value in mg.% on semilog paper.

NOTES.—Normal values: 65 to 100 mg.% (blood)

Adults: 40 to 70 mg. per 100 ml. (spinal fluid)

Children: 70 to 90 mg. per 100 ml. (spinal fluid)

The method outlined above for the determination of glucose in body fluids based on the technique of Somogyi and Nelson has been adapted and modified by Indiana University Clinical Laboratory Chemistry Department. By the use of copper sulfate and sodium tungstate, both the proteins and the nonsugar reducing substances present in the specimen are precipitated, leaving true sugar as the only reducing substance in the protein-free filtrate. The values thus obtained are approximately 10 to 20 mg.% lower than those of the Folin-Wu method of protein precipitation. Glucose present in the filtrate reduces copper in alkaline solution when heated. The cuprous copper so formed reacts with arsenomolybdate reagent to produce a stable blue color, the intensity of which varies directly with the amount of reducing substance present in the filtrate. According to Somogyi, when using copper sulfate and sodium tungstate, for protein precipitation, the excess copper is precipitated in the form of tungstate. The presence of copper in the filtrate does not affect the determination of glucose with alkaline copper reagents.

## 5-HYDROXYINDOLEACETIC ACID

(Urine)

**Reagents.** 1-Nitroso-2-naphthol, 0.1%.—To a 100-ml. volumetric flask add 0.1 g. of 1-nitroso-2-naphthol and dilute to 100 ml. with 95% ethyl alcohol.

**Nitrous Acid Reagent.**—This must be prepared just before using. Add 0.2 ml. of 2.5% sodium nitrite to 5 ml. of 2 N sulfuric acid.

**5-Hydroxyindoleacetic Acid (5-HIAA) Stock Standard.**—Weigh 50 mg. of 5-HIAA and dissolve in 500 ml. of distilled water. Add 25 drops of glacial acetic acid to keep the pH approximately 3. In this solution 1 ml. is equivalent to 100  $\mu$ g. 5-HIAA.

**Procedure.**—Obtain a 24-hour specimen of urine in a suitable container to which has been added 3 ml. of toluene and 25 ml. of glacial acetic acid prior to collection. Measure the total volume of the specimen and record. Place a 5-ml. aliquot of urine in a 50-ml. centrifuge tube. Into a second 50-ml. centrifuge tube place 5 ml. of water which will serve as a blank. To each tube add approximately 2 g. of sodium chloride and 25 ml. of ether. Place a number 6 rubber stopper in each of the centrifuge tubes and shake for 1 minute. Be sure the rubber stoppers are held in tightly; otherwise the expanding ether fumes will force the stopper out. Remove the rubber stoppers and centrifuge the tubes at 2000 r.p.m. for 2 minutes.

Place 20 ml. of the ether layer in a 125 ml. Pyrex suction flask, apply gentle suction and evaporate slowly to dryness with the flask immersed in a 59°C. water bath. To the residue in the suction flask add 4 ml. of distilled water. Into a suitable size test tube (large enough to hold 15 ml. of solution) place 2 ml. of the water extract. Add 1 ml. of nitrosonaphthol reagent and 1 ml. of the nitrous acid reagent. Mix well and place the tubes in a 59°C. water bath for 5 minutes. Remove the tubes from the water bath and add 10 ml. of ethyl acetate. Mix well and let stand 30 minutes at room temperature. Pipet approximately 2 ml. of the aqueous solution (bottom layer) into a small (12- by 75-mm.) cuvet, and read against a reagent blank in a spectrophotometer at 650 m $\mu$ . Obtain results from a calibration curve. The results obtained from the calibration curve are in milligrams per liter, so this must be corrected for the 24-hour volume.

**Calculations.**—

$$\frac{\text{Mg./liter} \times 24\text{-hour volume}}{1000} = \text{mg./24-hour specimen}$$

**Calibration Curve.**—Dilute 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, and 22.5 ml. of stock 5-HIAA standard to 25 ml. with distilled water. These dilute standards represent, respectively, 10, 20, 30, 40, 50, 60, 70, 80, and 90 mg. 5-HIAA per liter. Place 2 ml. of the dilute standards in suitable size test tubes and proceed as above, beginning with the nitrosonaphthol reagent. In another test tube place 2 ml. of water and treat the same as the dilute standards. This will represent the reference blank. Read the standards against the reference blank set at 100% transmittance at 650 m $\mu$ . Plot the results obtained on semilog paper.

**NOTES.**—The normal range is 2 to 9 mg. 5-HIAA per 24-hour specimen.

Of particular interest to the laboratory are those compounds which cause false positive or negative reactions. Those which produce false positive reactions are: aspirin, phenacetin, and Thorazine spansules. The color produced by the first two is stable and that produced by the Thorazine spansules fades in about 1 hour. Assuming an average urine excretion of 1500 ml., approximately 75 grains of aspirin or phenacetin or 1500 mg. of Thorazine

spansules would have to be ingested to produce false positive reactions. Thus, the incidence of false positives should be quite small.

False negatives, however, are not uncommon. In general, drugs of the chlorpromazine groups cause inhibition of the color development. For this reason it is important to include a control in the determination. If the control shows less color development than the standard, it may be assumed that the unknown is inhibited. Among those drugs found in our laboratories to cause inhibition are: Phenergan, Promethazine Hydrochloride, Mephentermine Sulfate, Thorazine, Trilafon, Compazine, Pacatal, and Sparine.

From the foregoing it can be seen that the patient should abstain from medications for 72 hours prior to the collection of urine for the test. The excretion of 5-hydroxyindoleacetic acid is not necessarily uniform over a 24-hour period. Therefore, the test should be performed on an aliquot of a 24-hour urine collection.

## 17-HYDROXYCORTICOSTEROIDS

(Urine)

**Procedure.**—Specimens to be assayed for 17-hydroxycorticosteroids should be collected without preservative but refrigerated during collection and storage.

Reducing sugars, in amounts exceeding 0.25%, will seriously interfere with the determination. All specimens should be tested for reducing sugar; if reducing sugar is present, one of the following techniques should be used:

a. **Removal of Urinary Glucose with Yeast.**—This method will succeed if glucose is the reducing sugar; it is the simpler method and should be tried first.

Weigh about 1 g. of yeast. Wash twice with 5 ml. of water and discard the water each time after centrifuging briefly. Suspend yeast in 3 ml. of water, add 2 ml. of the suspension to 20 ml. of the urine specimen and incubate until a negative sugar test is obtained. Centrifuge and use supernatant for the assay.

b. **Extraction of the Steroid Conjugates.**—This method has the advantage of removing all sugars as well as substances interfering with this and other steroid methods; it is, however, time consuming.

Dilute a 15-ml. aliquot of the specimen with 15 ml. of distilled water. Add 15 g. of ammonium sulfate to the diluted urine and extract the solution four times with 25 ml. of an ethanol-ether mixture (1:3). Combine the ethanol-ether phases, evaporate to dryness under reduced pressure, and dissolve the residue in 15 ml. of 0.2% urea solution.

In order to prevent excessive evaporation, the specimens are kept in ice water between manipulations (purification of ether extract).

Perform the analysis in duplicate on each specimen. Check for the presence of sugar. If present, remove with yeast or extract. To a 5-ml. aliquot of specimen (use 5 ml. of urea solution, 5.5 ml. after yeast treatment) in a test tube to which a polyseal screwcap can be adapted, add 0.25 ml. fresh sodium borohydride solution (100 mg. per ml.) and allow the reduction to proceed for at least 1 hour (or overnight) in the open tube. Add 5 ml. of glacial acetic acid; after 10 minutes, add 1.0 g. of sodium bismuthate, cap the tube, and shake mechanically in the dark for 2 hours. (Wrap the test tube rack in dark cloth or enclose in a box.) Add 3 ml. of 20% (wt./vol.) sodium metabisulfite and shake for 1 minute. Add 3 ml. of concentrated hydrochloric acid, shake the stoppered tube, place in a boiling water bath for 12 minutes and allow to cool to room temperature in ice water.

Add 25 ml. of diethylether to each tube and shake mechanically for 2 minutes; aspirate off the aqueous layer. Add 5 ml. of *N* hydrochloric acid and shake for 15 seconds; cool in ice water and aspirate off the aqueous layer. Add 5 ml. of 5 *N* sodium hydroxide and shake for 1 minute; cool in ice water and aspirate off the

Obtain about 15 ml. of oxalated blood, centrifuge at low speed, remove and discard about 2 ml. of the supernatant plasma, and thoroughly remix the specimen. Set up the following dilutions of blood:

<i>Tube No.</i>	<i>Blood, ml.</i>	<i>Saline, ml.</i>
1	2	0
2	2	0.5
3	2	1
4	2	2
5	2	4
6	2	8

NOTE.—Saline is 0.85% sodium chloride solution.

Mix thoroughly and sample, in triplicate, for the determination of iron, oxyhemoglobin, and cyanmethemoglobin.

**Oxyhemoglobin.**—Blood is laked in 0.04% ammonium hydroxide and shaken to oxygenate the hemoglobin.

Prepare tubes containing 5.0 ml. of 0.04% ammonium hydroxide. Add 0.02 ml. of capillary or oxalated blood, rinsing the pipet at least three times. Stopper; shake for 10 seconds. Read in a spectrophotometer at 540 m $\mu$ . Read equivalent hemoglobin from the calibration curve or table.

**Cyanmethemoglobin.**—Blood is laked, and the hemoglobin is converted to cyanmethemoglobin by the cyanide in the diluting fluid.

Prepare tubes containing 5.0 ml. of the cyanide reagent. Add 0.02 ml. of capillary or oxalated blood, rinsing the pipet at least three times. Mix thoroughly and let stand for at least 10 minutes before reading. Read in a spectrophotometer, wavelength 540 m $\mu$ . Read equivalent hemoglobin from the calibration curve or table.

**Total Iron in Whole Blood.**—The iron is liberated by treating whole blood with concentrated sulfuric acid and potassium persulfate. The protein is precipitated, and the iron concentration in the protein-free filtrate is measured by means of the thiocyanate reaction. The concentration of hemoglobin in the specimen is then calculated according to the following formula:

$$\text{Hemoglobin, g./100 ml.} = \frac{\text{iron, mg./100 ml.}}{3.34}$$

Dilute 10.0 ml. of the stock standard iron solution to 100 ml. in a volumetric flask. Mix. Transfer 0, 1.0, 2.0, 3.0, 5.0, 8.0, and 10.0 ml. to cylinders graduated at 20 ml. These standards represent 0, 10, 20, 30, 50, 80, and 100 mg. of iron per 100 ml. of blood when exactly 100 mg. of iron wire are used in preparing the standard. Add 0.4 ml. of concentrated sulfuric acid and dilute each to 20 ml. with distilled water. To each cylinder, add 1 ml. of saturated potassium persulfate solution and 4 ml. of 3 *N* potassium thiocyanate solution. Stopper, mix, and read the transmittance (*T*) in a spectrophotometer, wavelength 540 m $\mu$ . Construct an iron calibration curve on semilogarithmic paper, plotting *T* against iron concentration.

Using the six tubes of diluted oxalated blood, determine the iron concentration of each specimen as follows: Transfer 0.5 ml. of blood to a dry 50-ml. volumetric flask. Add 2 ml. of concentrated sulfuric acid. Mix thoroughly by swirling. Add 2 ml. of saturated potassium persulfate solution, mix, and dilute to about 25 ml. with distilled water. Add 3 ml. of 10% sodium tungstate solution, mix, cool to room temperature, and dilute to 50 ml. with distilled water. Mix thoroughly by



inversion and filter. Transfer 10 ml. of the filtrate to a dry test tube or flask and add 10 ml. of distilled water. Add 1 ml. of saturated potassium persulfate and 4 ml. of 3 *N* potassium thiocyanate. Stopper, mix, and read in the spectrophotometer, wavelength 540 m $\mu$ . Read the equivalent hemoglobin value from the previously drawn calibration curve. Read each sample of oxalated blood as cyanmethemoglobin and as oxyhemoglobin. Since the hemoglobin value of each is now known, draw a calibration curve for each method, plotting the *T* reading for that method against the known hemoglobin concentration of each sample. Charts can be made from the curves.

## PROTEIN BOUND IODINE

(Serum)

**Reagents.**—All water used must be at least doubly distilled and all reagents of highest purity.

**0.02 *N* Ceric Ammonium Sulfate Solution** (G. Frederick Smith Chemicals).—Dissolve 25.30 g. of ceric ammonium sulfate in 1 liter of water plus 460 ml. of 7 *N* sulfuric acid. When the solution is clear, make it up to 2 liters with water.

**0.1 *N* Sodium Arsenite Solution.**—Dissolve 12.993 g. of sodium arsenite reagent grade in 1 liter of water or dissolve 4.947 g. of arsenic trioxide (As<sub>2</sub>O<sub>3</sub>) reagent grade in 25 ml. of 4% sodium hydroxide (1 *N*) and warm to hasten solution. This solution is diluted with about 300 ml. of water and diluted with about 4 ml. of 7 *N* sulfuric acid or until the solution is slightly acid to litmus paper. The solution is then made to 1 liter with water.

**Stock Iodine Solution.**—Dissolve 130.8 mg. of potassium iodide reagent grade of highest purity, desiccator dried, in 1 liter of water. This stock solution contains 100  $\mu$ g. per ml. of iodine.

**Standard Iodine Solution.**—(a) Solution containing 0.04  $\mu$ g. of iodine per milliliter of solution is prepared by diluting 2 ml. of stock solution to 500 ml. with water and then diluting 5 ml. of the diluted stock to 50 ml.

(b) Solution containing 0.01  $\mu$ g. of iodine per milliliter of solution is prepared by adding 1 ml. of 0.04  $\mu$ g. standard with 3 ml. of water.

**Reagent Blank.**—To an Erlenmeyer flask, add 8 ml. of zinc sulfate, 8 ml. of 4 *N* sodium carbonate, 16 ml. of 7 *N* sulfuric acid, 16 ml. of 2 *N* hydrochloric acid, 8 ml. of redistilled water. Mix well. All effervescence must cease before pipetting.

**Procedure.**—One milliliter of serum is pipetted into each of two numbered ashing tubes (15- by 85-mm. Pyrex test tubes) and diluted with 6 ml. of redistilled water. One milliliter of 10% zinc sulfate solution and 1 ml. of 0.5 *N* sodium hydroxide solution are added. The contents of each tube are mixed with a glass stirring rod (3 mm. in diameter). Any material adhering to the rod can be removed by washing the rod down with distilled water from a wash bottle. The tubes are then centrifuged for 10 minutes at 2000 r.p.m. and the supernatant fluid is poured off. Seven milliliters of water are added and the precipitated protein is resuspended by means of the stirring rods originally used for each tube. Centrifugation is again carried out for 10 minutes at 2000 r.p.m. and the supernatant discarded. This washing process is repeated two more times, making a total of three washings. After the last supernatant has been poured off, 0.5 ml. of 4 *N* sodium carbonate is added to each tube and thoroughly stirred into the precipitate with the same stirring rods used in the washings. Removal of material clinging to the rods is accomplished by rinsing each rod with an additional 0.5 ml. of 4 *N* sodium carbonate.

(Total volume of  $\text{Na}_2\text{CO}_3$  is 1.0 ml.) The tubes are then placed in an oven maintained at  $100^\circ\text{C}$ . They are allowed to remain in the oven for a period of 12 to 18 hours, or until the contents of the tubes are thoroughly dry.

The tubes are placed in Pyrex beakers and then in a muffle furnace at  $600^\circ \pm 25^\circ\text{C}$ . for at least  $2\frac{1}{2}$  hours of ashing. After this, the tubes are removed and allowed to cool. Two milliliters of 2 *N* hydrochloric acid are added with caution to avoid excessive effervescence. Then 2 ml. of 7 *N* sulfuric acid and 3 ml. of distilled water are added. The contents of the tubes are stirred with a stirring rod. The tubes are then centrifuged for 10 minutes at 2000 r.p.m. to pack any insoluble material. For each sample tube, a large cuvet (19 by 105 mm.) is used. To each cuvet, add 5 ml. of distilled water and a 3-ml. aliquot of the supernatant solution from the corresponding sample tube. To each cuvet, add 0.5 ml. of 0.1 *N* sodium arsenite solution. Mixing is carried out by flapping or twirling the tubes.

The cuvet and ceric ammonium sulfate in a separate tube are placed in a constant-temperature water bath maintained at  $39^\circ \pm 1^\circ\text{C}$ . for 10 minutes to come to temperature equilibrium. Using an Ostwald-Folin, blow-out pipet, 1 ml. of ceric ammonium sulfate solution is added to each tube at precisely 30- or 60-second intervals. A stop watch is used to assure accurate timing and the tubes are kept in the water bath during the addition of ceric ammonium sulfate. Twenty minutes after the ceric solution has been added to the first tube, readings are taken on the spectrophotometer at 420  $\text{m}\mu$ , leaving the same time interval between readings as was allowed between additions of the ceric ammonium sulfate. Use water as a reference blank. Read per cent transmittance, record readings, average the duplicates, and calculate.

Calculations.—Check calibration curve to obtain curve reading for the particular per cent transmission.

$$\text{Curve reading} \times \frac{7}{3} \times 100 = \mu\text{g. 100 per ml.}$$

Calibration Curve.—A blank and three standards (0.01, 0.04, and 0.08  $\mu\text{g. per ml.}$ ) are prepared as follows: 5 ml. of water are added to the blank tubes; 4 ml. of water and 1 ml. of 0.01 standard are added to the "0.01" tubes; 4 ml. of water and 1 ml. of 0.04 standard solution are added to the "0.04" tubes; and 3 ml. of water and 2 ml. of 0.04 standard solution are added to the "0.08" tubes. To keep the pH and composition of the blank and standards the same as those of the samples, 3 ml. of reagent blank are added to each tube. Therefore, all the tubes should contain 8 ml. of solution. Proceeding with the sodium arsenite step of the main procedure, continue as directed. Plot the per cent transmittance against the iodide concentration. New solutions require a new curve.

Notes.—Extreme accuracy and carefulness are necessary in the preparations of all reagents. All glassware must be acid washed and free from contamination. Temperature of the muffle furnace should not rise above  $625^\circ\text{C}$ . because the glass tubes will begin to melt. Loss of iodine occurs above this level.

Normal values:	Adults	5-9 $\mu\text{g. per 100 ml.}$
	Children	4-8 $\mu\text{g. per 100 ml.}$

Unless iodine or thyroid extract therapy is discontinued for ten days to two weeks prior to drawing the specimen, these drugs will interfere with true thyroid activity. Diagnostic X-ray studies employing organic iodine as contrast media (e.g., Diodrast, Lipiodal, Iodabon, etc.) can give false high readings for six months to a year after administration. Results of 25  $\mu\text{g.}$  are almost always traceable to this source. Iodine used for sterilizing the skin preparatory to venipuncture can also cause false elevations.

## IRON

(Serum)

**Reagents. Color Reagents.**—Weigh out 100 mg. of bathophenanthroline (G. Frederick Smith Chemical Company, Columbus, Ohio; c.p. grade). Add 0.5 ml. of iron-free chlorosulfonic acid and heat over the flame of a microburner for 30 seconds. Cool, carefully add 10.0 ml. of contaminate-free distilled water, and warm in a water bath with stirring to dissolve all solid material. Dilute 3.0 ml. of the reagent to 100 ml. with 45% sodium acetate solution, filter off any insoluble material, and store in glass-stoppered brown bottle. The reagent appears to be stable for several months stored in such a bottle.

**Iron Stock Standard.**—Weigh out 100 mg. of analytical grade iron wire, dissolve in 50% vol./vol. *sulfuric acid solution* and dilute with water to 1 liter. The sulfuric acid should be in excess.

**Iron Working Standards.**—Dilute 0.0, 1.0, 2.0, 3.0, and 4.0 ml. of the iron stock standard to 100 ml. with distilled water. These correspond to concentrations of 0 to 400  $\mu\text{g.}$  per 100 ml.

**Procedure.**—Pipet one 1.0-ml. sample of serum into a clean, dry, glass-stoppered centrifuge tube. Prepare blank for the analyses by substituting 1.0 ml. of contaminate-free distilled water for the serum, 0.5 ml. of contaminate-free distilled water for the trichloroacetic acid, and proceed as below for serums. Prepare standard by pipetting 1.0 ml. of the iron working standard into tube and treat as described for the blank samples.

Add 1.0 ml. of 1 *N* HCl to the tube, mix and heat for 5 minutes in a near boiling water bath. Cool, and add 0.5 ml. of 10% trichloroacetic acid and mix thoroughly with a clean glass rod or by vigorously shaking the stoppered container. Centrifuge at 3500 to 4000 r.p.m. for 15 minutes. Pipet 1 ml. of the clear supernatant solution into a clean cuvet (10 by 75 mm.). Add a small spatula tipful (approximately 10 mg.) of solid ascorbic acid to each of the cuvetts, and mix well. (The amount of ascorbic acid added is not critical.) Add 0.2 ml. of bathophenanthroline color reagent, and mix well. Read the sample against its appropriately prepared blank at 535 millimicrons for the red iron complex.

**Calculations.**—

$$\text{Iron } \mu\text{g. per 100 ml.} = \frac{\text{absorbance of unknown} \times \text{conc. of standard}}{\text{absorbance of standard}}$$

Same precautions should be followed here as in the serum copper procedure.

**NOTE.**—Normal values: 50 to 100  $\mu\text{g.}$  per 100 ml. of serum.

## 17-KETOSTEROIDS

(Urine)

**Reagents. Diethylether, A. R.**—Use one-pound tins. Ether containing peroxides should not be used for steroid analysis.

**Test:** Dissolve a few crystals of potassium iodide in 5 ml. of water, add an equal volume of the ether to be tested and shake for 1 minute. If a yellow color develops the ether contains peroxides. It is advisable to test any ether tin that has been open for more than a month before it is used. If satisfactory ether cannot be

obtained, purify as follows: Shake with 0.8 *M* ferrous sulfate in 0.4 *N* sulfuric acid ( $3 \times 100$  ml. per liter) wash with water ( $2 \times 50$  ml. per liter) and distill from an all-glass still in a fume hood.

**Methanol, Acetone Free (Merck No. 7168).**—Purify as follows: To 1200 ml. of methanol add 2 g. of silver nitrate dissolved in 5 ml. of distilled water. Then add 5 g. of potassium hydroxide dissolved in 25 ml. of warm methanol (25 ml. 4 *N* methanolic potassium hydroxide if available). Filter the mixture under suction through a bed of Celite and transfer the filtrate to an all-glass still. Discard the first 100 to 150 ml. and collect about 800 ml. of distillate (b.p.  $65^\circ \pm 1^\circ$ ).

**Ethylene Glycol Monomethyl Ether ("Methyl Cellosolve").**—Commercial methyl Cellosolve (Carbide and Carbon Company, technical grade or Dowanol No. 7, Dow Chemical Company) is purified as described for methanol (b.p.  $124^\circ \pm 1^\circ$ ); reagent grade methyl Cellosolve (Merck No. 43713, "Karl Fischer Diluent") does not have to be purified.

***m*-Dinitrobenzene.**—Dissolve 30 g. of *m*-dinitrobenzene (Eastman-Kodak No. 99) in 250 ml. of methanol (reagent grade, not redistilled) on the steam bath. Add 30 ml. of 5 *N* sodium hydroxide and allow the precipitate to stand for 30 minutes. Filter the crystalline material on a Büchner funnel, wash with distilled water on the funnel until the washes are colorless, and suck dry. Redissolve the crystals in 150 ml. of redistilled methanol, add 250 ml. of water, and allow the precipitation to go to completion in the dark. Filter the crystals and wash as previously; blot dry and store in a vacuum desiccator in the dark over calcium chloride.

***m*-Dinitrobenzene, 1% Solution.**—Prepare a 1% solution of purified *m*-dinitrobenzene in purified methyl Cellosolve (wt./vol.). Store in a dark bottle; keep in the refrigerator when not in use.

**Potassium Hydroxide, A. R.**—A low carbonate content is preferable.

**Methanolic Potassium Hydroxide.**— $4.0 \pm 0.15$  *N*. Prepare 60 ml. of reagent as follows: Measure 60 ml. of purified methanol into a 125-ml. Erlenmeyer flask containing a small magnetic stirring bar and weigh the flask roughly on a trip balance. Add 17 g. of potassium hydroxide pellets directly into the flask and stir to dissolve the pellets. Filter under suction through Whatman No. 50 filter paper, measure the clear filtrate, and store in a polyethylene bottle. Dilute a 2-ml. aliquot with 18 ml. of distilled water and titrate against normal oxalic acid using phenolphthalein as an indicator. Adjust the normality if necessary.

**Standard.**—Androsterone is the preferable standard, but dehydroepiandrosterone may be substituted if androsterone from Sigma Chemical Company is not available.

**Stock Solution.**—The stock solution contains 2.5 mg. per ml. in redistilled methanol and is stored in the freezing unit of the refrigerator.

**Working Standard.**—The working standard contains 100  $\mu$ g. per ml. and is made by 2:50 dilution of the stock solution with redistilled methanol; it is kept in the refrigerator and allowed to come to room temperature before use.

**Procedure.**—Specimens to be assayed for 17-ketosteroids should be collected without preservative but refrigerated during collection and storage. Specimens preserved with hydrochloric acid (15-ml. concentrated acid per liter specimens) are adequate for 17-ketosteroids, but not for corticosteroid assays. A 30-ml. (1 ounce) aliquot is sufficient for ketosteroid analysis. Only alkali- and detergent-free glassware should come in contact with the color reagent. In order to prevent excessive evaporation, the specimens are kept in ice water between manipulations. Manual contact with the tubes is kept to a minimum.

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Perform the analysis in duplicate on each specimen. Pipet a 5-ml. aliquot of the specimen into a test tube to which a polyseal screwcap can be adapted. Add 1 ml. of hydrochloric acid and cap the tube. Place in a boiling water bath for 12 minutes, then allow to cool to room temperature in ice water.

Add 25 ml. of diethylether and shake mechanically for 2 minutes; aspirate off the aqueous layer. Add 5 ml. of 1 *N* sodium hydroxide and shake by hand for 15 seconds; allow the aqueous layer to separate and aspirate it off. Add 20 to 30 pellets of sodium hydroxide, stopper tightly, and shake mechanically in a horizontal position for 10 minutes. Centrifuge at 1500 r.p.m. for 5 minutes and filter rapidly through fluted filter paper into a large, clean test tube. Measure a 10.0-ml. aliquot of the filtrate in a pipet and aspirate off the balance of the filtrate. Place the 10.0-ml. aliquot back in the test tube and evaporate it to dryness in a 55°C. water bath. Add 0.5 ml. of methanol to the dry residue, bring all of the residue into solution by careful rotation of the tube. Evaporate the methanol (specimens, blank, standards) to dryness in a boiling water bath. At this time prepare a blank and standards by pipetting into large, clean test tubes the following:

<i>Tube for:</i>	<i>Working Standard ml.</i>	<i>Methanol, ml.</i>
Reagent blank.....	—	0.5
10 µg. standard.....	0.1	0.4
30 µg. standard.....	0.3	0.2
50 µg. standard.....	0.5	—

Add three parts of 4.0 *N* methanolic potassium hydroxide to four parts of 1% *m*-dinitrobenzene immediately before use; prepare about 20% in excess of the amount needed. Add 0.7 ml. of this reagent mixture to the bottom of each tube and allow the color to develop under uniform conditions at room temperature. After exactly 1 hour, add 5 ml. of methyl Cellosolve, and measure the absorbance at 440, 520 and 600 *m*µ (Beckman B or DU) or at 520 *m*µ (Coleman) against the reagent blank.

**Calculations.** *Beckman B or DU.*—Calculate the corrected absorbance:

$$A_c = 2A_{520} - (A_{440} + A_{600})$$

Plot  $A_c$  of the standards on linear graph paper and determine the concentration of the specimens  $C_x$  equals micrograms per 2 ml. of urine from the plot:

$$\text{Mg./specimen} = \frac{1}{2}C_x \times \text{specimen volume (liters)}.$$

**NOTE.**—If  $A_{440}$  is nearly equal to or greater than  $A_{520}$ , the determination should be repeated.

**Coleman.**—Plot the per cent transmittance of the standard on semilogarithmic paper and determine the concentration of the specimen ( $C_x$ ) from that plot:

$$\text{Mg./specimen} = \frac{1}{2}C_x \times \text{specimen volume (liters)}.$$

**NOTES.**—Normal Values (mg. per 24 hours), read at 520.

<i>Age (Years)</i>	<i>Less 2</i>	<i>2-5</i>	<i>5-10</i>	<i>10-15</i>	<i>15-60</i>	<i>60-90</i>
Male.....	0.5-1.5	1-3	3-6	6-15	10-20	20-5
Female.....	0.5-1.5	1-3	3-6	5-11	5-15	13-3

When read at three wavelengths, the values obtained are about 25% lower, due to elimination of contaminants such as 3-, 11-, or 20-ketosteroids.

The water-soluble conjugates (glucuronides, sulfates) or the major urinary steroids (androsterone, etiocholanolone, dehydroepiandrosterone, 11-oxygenated 17-ketosteroids) are hydrolyzed with concentrated hydrochloric acid under conditions designed to provide the maximal hydrolysis compatible with a minimal destruction of the steroids.

The low toxicity and the low boiling point of diethylether make it the solvent of choice for the extraction of the liberated steroids. Purification of the extract with 1 *N* sodium hydroxide and sodium hydroxide pellets is so effective that urinary blanks may be neglected.

The ratio of *m*-dinitrobenzene to potassium hydroxide is a critical feature of the colorimetric procedure (Zimmermann reaction); by mixing adequate proportions of the two reagents immediately before use and pipetting the mixture into each tube, variations in the ratio of the two reagents are avoided. The use of alcoholic potassium hydroxide reduces the formation of nonsteroidal Zimmermann chromogens.

The addition of ethylene glycol monomethyl ether (methyl Cellosolve) to the reacting mixture dilutes the KOH sufficiently to stop the reaction. In addition, the solvent dilutes the colored mixture to bring it into an optimal range for the determination of absorbance.

It has been found that if the Beckman DU or B spectrophotometer is employed, the absorbance of the mixture should be determined at three wavelengths in order to eliminate interfering chromogens such as 3- or 20-ketosteroids and nonsteroidal substances. If the Coleman spectrophotometer is used, a determination at one wavelength seems satisfactory.

The specific name brands of reagents are designated because experience has shown that they produce the most uniform and constant results. If substitutions are made, there may be considerable loss of accuracy and precision.

## LIPASE

(Serum, Duodenal Contents)

**Reagents. Olive Oil Emulsion.**—To 93 ml. of distilled water, add 0.2 g. of sodium benzoate and 7 g. of gum arabic (USP). Mix in a blender at low speed until dissolved. Slowly add 93 ml. of olive oil (Fisher, Best, USP, Fisher Scientific Company, Catalog No. 0-111) and continue mixing with a blender at low speed for an additional 3 minutes. Then mix for 5 minutes at high speed. This reagent should be stored at 10° to 14°C. Freezing or exposure to excessive heat will destroy the emulsion. Shake well before using. The reagent is stable for six months and should not be used thereafter.

**Thymolphthalein.**—Dissolve 1 g. in ethanol and dilute to 100 ml. with ethanol.

**Barbiturate Buffer, pH 8.0.**—Sodium diethyl barbiturate 0.8583 g. and 0.4183 g. of diethyl barbituric acid are dissolved in approximately 90 ml. of hot water. After cooling, the solution is transferred to a 100-ml. volumetric flask and diluted to the mark with water. Toluene or chloroform (two to three drops) are added as preservative. The reagent is stable at refrigerator temperature.

**Procedure. Serum.**—Into each of two test tubes, pipet 2.5 ml. of water, 3.0 ml. of olive oil emulsion, and 1.0 ml. barbiturate buffer pH 8.0. [The barbiturate buffer can be replaced by a 0.2 *M* tris(hydroxymethyl)aminomethane buffer pH 8.0 (Sigma Chemical Company, St. Louis 18, Mo.)]. This buffer has a slightly better buffer capacity that results in a slightly higher rate of hydrolysis. The substance should be anhydrous before the sample is weighed for the preparation of the buffer. The blank titration for this buffer is higher than the value for the barbiturate buffer.

Into one of the two tubes, pipet 1.0 ml. of serum. Mark this tube "test" and the other tube "blank." Shake both tubes vigorously (at least 5 seconds). Pipet

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1.0 ml. of serum into a 50-ml. Erlenmeyer flask. This flask with serum must be stored in the refrigerator ( $4^{\circ}$  to  $10^{\circ}\text{C}.$ ). Incubate the "test" and the "blank" in a water bath at  $37^{\circ}\text{C}.$  for 6 hours. (In case of suspected acute pancreatitis, it is recommended that the test be performed in duplicate and that one test be titrated after 3 hours of incubation.) An abnormal level of lipase in serum after 3 hours has obvious diagnostic importance.

Transfer the contents of "blank" into the Erlenmeyer flask containing the serum. Transfer the contents of "test" tube into a clean 50-ml. Erlenmeyer flask. Pipet 3.0 ml. of ethyl alcohol, 95%, into the "blank" and "test" tubes, shake, and add to respective Erlenmeyer flasks. Add four drops of thymolphthalein indicator to the "blank" and "test." Titrate to a light blue color with 0.05 *N* sodium hydroxide. (The "blank" and "test" should be titrated to the same color intensity.) Subtract "blank" value from "test" value. Units of lipase in serum are equivalent to milliliters of 0.05 *N* sodium hydroxide used to neutralize the liberated free fatty acid under the conditions of the test. The results ranging up to 1.0 units are considered to be within normal limits.

**Duodenal Contents.**—Make a 1:50 dilution of duodenal contents as follows: 1 ml. duodenal contents is made up to 50 ml. by adding 10 ml. of the buffer and distilled water. Proceed as for the serum procedure.

**NOTES.**—Units of lipase in duodenal contents are equivalent to  $50 \times$  milliliters of 0.20 *N* sodium hydroxide used to neutralize the liberated free fatty acids under the conditions of the test. The results ranging up to 267 units are considered to be within normal limits.

The sample to be analyzed is refrigerated from the time it is obtained from the patient to the time the analyses are to be made. Repeated studies have indicated that there is no significant alteration in enzyme activity of duodenal contents during a period of 24 hours, provided the sample is not strongly acid due to contamination with gastric juice. In such cases the results are quite unreliable even though the analyses are made immediately.

### TOTAL LIPIDS

(Serum, Plasma, Feces)

**Reagents. Acid Molybdate Solution.**—Add 83 ml. of concentrated  $\text{H}_2\text{SO}_4$  to about 400 ml. of water. Dissolve 25 g. of  $(\text{NH}_4)_2\text{MoO}_4$  in the acid and then dilute to 1 liter.

**Reducing Agent: 1-amino-2-naphthol-4-sulfonic Acid (0.05%).**—Dissolve 29.2 g. of  $\text{NaHSO}_3$  and 1 g. of  $\text{Na}_2\text{SO}_3$  in 200 ml. of water. Add 0.2 g. of powdered 1-amino-2-naphthol-1-sulfonic acid and shake until dissolved. Filter with activated charcoal if colored, and keep in a brown bottle.

**Phosphate Standard (10 mg. per 100 ml.).**—Make up to 1 liter with water 438 g.  $\text{KH}_2\text{PO}_4$  (dried at  $80^{\circ}\text{C}.$  overnight and cooled in a desiccator). Keep under toluene.

**Procedure. Serum and Plasma Total Lipids.**—One milliliter of fasting serum or plasma followed by 1 ml. of ethyl alcohol is introduced into a 100-ml. Erlenmeyer flask fitted with a ground-glass stopper or cork rubbed in silicone grease; 20 ml. of chloroform and 20 ml. of 10% sulfuric acid are added. The mix is shaken in a shaking machine for 30 minutes. It is transferred to a 60-ml. test tube, and then centrifuged for 15 minutes at 2000 r.p.m. The aqueous layer is aspirated off and discarded. The protein button is pushed aside and the chloroform layer is passed through porous filter paper to dry. A 10-ml. aliquot of the chloroform layer is

placed in a weighed 25-ml. Erlenmeyer flask, evaporated to dryness on a steam bath, and then dried in a 70°C. oven to constant weight. The beaker is weighed.

$$\text{Mg. lipid found} \times 200 = \text{total lipid (mg. per 100 ml.)}$$

NOTE.—Total lipids comprise a complex mixture of substances, including neutral fat, fatty acids, cholesterol, phospholipids, and numerous other fatty materials present in lesser amounts, such as carotene, vitamins A and D, and steroid hormones. Here we are interested in the determination of total lipids, phospholipids (lipid phosphorus), and fatty acids. In adults, the total lipid values normally range from 400 to 700 mg. per 100 ml. In children values range from 300 to 600 mg. per 100 ml.

**Lipid Phosphorus.**—0.5 ml. of the chloroform layer, as extracted above, may be evaporated to dryness in a test tube. Add 0.05 ml. of concentrated  $\text{H}_2\text{SO}_4$ . Digest at 120°C. adding 0.1-ml. portions of 30%  $\text{H}_2\text{O}_2$  until the carbon ceases to form and the solution clears. Make up to 2 ml. Take a 1-ml. aliquot and add 0.5 ml. of acid molybdate reagent, mix, and then add 0.5 ml. of reducing agent. Mix well and allow to stand for 30 minutes. Read in a spectrophotometer at 660  $\mu$ . Take 0.1 ml. of distilled water for the blank and 0.1 ml. of 10 mg. per 100 ml. standard and treat both as for the unknown.

$$\frac{\text{Absorbance of the unknown}}{\text{Absorbance of the standard}} \times 7.5 = \text{mg. of lipid phosphorus per 100 ml. of serum.}$$

NOTE.—Normally, plasma or serum contains 9 to 10 mg. of lipid phosphorus per 100 ml. of serum.

**Fatty Acid Determination.**—The residue in the Erlenmeyer flask from the total lipid determination is dissolved in 2 ml. of 1% alcoholic KOH and heated on a steam bath for 15 minutes. Three milliliters of water are added and the solution is acidified to congo red paper by drop-by-drop addition of concentrated HCl; 15 ml. of petroleum ether (b.p. 60°C.) are added, and the mixture is shaken for 20 minutes on the Kahn shaker. Decant the solution into a small separatory funnel, wash in with 5 ml. of water and discard the lower layer. Wash the petroleum ether layer twice with 5-ml. portions of water. Filter the petroleum ether layer through filter paper into a small beaker to dry, and wash through with 5 ml. of petroleum ether. Evaporate the petroleum ether to dryness, pick up the residue in 2 ml. of ethanol, and titrate with 0.50 N KOH, using phenolphthalein as an indicator. Titration will be of the order of 1 ml., and an ultra-microburet is used.

Titrate 2 ml. of ethanol as the blank, to be subtracted from the titration of the unknown.

$$\text{Ml. titration (corrected for blank)} \times 750 = \text{milliequivalents per liter of fatty acid}$$

$$\text{Milliequivalents per liter} \times 27.7 = \text{mg. fatty acid per 100 ml.}$$

NOTE.—Assuming an average molecular weight of 277, the approximate normal range of concentrations of fatty acids in serum is 200 to 450 mg. per 100 ml.

**Feces.**—Place the sample in a glass container in a 60° to 70°C. oven overnight to dry. Remove to a mortar, and grind with the pestle. Weigh a 500-mg. aliquot into a 15-ml. test tube. Add 5 ml. of 1 N HCl and 5 ml. of a 1:1 petroleum ether (b.p. 70° to 90°C.)—fat-free diethylether solution. Add one drop of 95% ethyl alcohol. Cork with silicone greased stoppers. Shake in a horizontal position in the Kahn shaker for 25 minutes. Centrifuge and aspirate as much of the



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1.0 ml. of serum into a 50-ml. Erlenmeyer flask. This flask with serum must be stored in the refrigerator (4° to 10°C.). Incubate the "test" and the "blank" in a water bath at 37°C. for 6 hours. (In case of suspected acute pancreatitis, it is recommended that the test be performed in duplicate and that one test be titrated after 3 hours of incubation.) An abnormal level of lipase in serum after 3 hours has obvious diagnostic importance.

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**NOTES.**—Units of lipase in duodenal contents are equivalent to 50 × milliliters of 0.20 N sodium hydroxide used to neutralize the liberated free fatty acids under the conditions of the test. The results ranging up to 267 units are considered to be within normal limits.

The sample to be analyzed is refrigerated from the time it is obtained from the patient to the time the analyses are to be made. Repeated studies have indicated that there is no significant alteration in enzyme activity of duodenal contents during a period of 24 hours, provided the sample is not strongly acid due to contamination with gastric juice. In such cases the results are quite unreliable even though the analyses are made immediately.

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top layer as possible into a 25-ml. weighed Erlenmeyer flask. Add 5 ml. of petroleum ether-ether solution to the residue in the test tube. Cork and shake by hand. Centrifuge again and transfer the supernatant into a weighed Erlenmeyer flask.

Evaporate the solution to dryness on a steam bath or 100°C. air bath. Weigh the flask with the lipid.

$$(\text{Wt. flask} + \text{fat}) - (\text{wt. flask empty}) = \text{mg. fat/500 mg. stool}$$

$$\frac{\text{Mg. lipid in 500 mg. stool}}{5} = \% \text{ fat in stool}$$

If free fatty acid content is desired, dissolve the lipid residue in 10 ml. of 95% ethanol. Heat the flask on a steam bath to help the dissolving. While hot, add one drop of phenolphthalein and titrate with 0.1 *N* NaOH. The calculations then become

$$\frac{\text{Ml. titration} \times \text{normality of alkali} \times 268 \times 100}{\text{Wt. of lipid in mg.}} = \% \text{ fatty acids of total lipids}$$

268 being the average molecular weight of stool fatty acids.

NOTES.—Values in normal adults on an unrestricted diet do not exceed 17% of the stool's dry weight. Most commonly, values are below 10%. In infants, values less than 20% are considered normal. Approximately 75 to 90% of the fecal fat is free fatty acid or soap. In this procedure, the soap is converted to free fatty acid.

### METHEMOGLOBIN

(Whole Blood)

**Reagents.** Phosphate Buffer, 0.066 . . . *M* (pH 6.6).—Dissolve 9 g. of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and 5.7 g. of anhydrous  $\text{KH}_2\text{PO}_4$  in distilled water and dilute to a volume of 1 liter. To prepare 0.0166 . . . *M* buffer (pH 6.6), dilute 1 volume of the 0.066 . . . *M* solution with 3 volumes of distilled water.

**Neutralized Sodium Cyanide.**—Add 1 volume of 12% acetic acid (12 ml. of glacial to 100 ml. with distilled water) to 1 volume of 10% sodium cyanide. The reagent should be prepared in a hood, adding the acid to the cyanide. The solution should be used within an hour after preparation and dispensed from a dropper bottle.

**Procedure.**—Add 0.1 ml. of capillary or of oxalated venous blood collected under oil to 10 ml. of 0.0166 . . . *M* phosphate buffer. Mix and let stand 5 minutes. Read absorbance at 635  $m\mu$ , using distilled water as the blank. Absorbance reading is  $D_1$ . Add one drop of neutral sodium cyanide. Mix and let stand 2 minutes. Read at 635  $m\mu$ . Absorbance reading is  $D_2$ .

$$(D_1 - D_2) \times F_m = \text{g. of methemoglobin per 100 ml. of blood.}$$

**Determination of  $F_m$ .**—No. 1 tube (unknown): 9.9 ml. 0.0166 . . . *M* phosphate buffer + 0.1 ml. 5% potassium ferricyanide solution. No. 2 tube (blank): 10 ml. 0.0166 . . . *M* phosphate buffer + 0.1 ml. 5% potassium ferricyanide solution. Add 0.1 ml. of blood to the unknown. The hemoglobin concentration of this blood should be determined by the Wong iron method (p. 1098). Mix and allow to stand 2 minutes. Read  $D_1$ , at 635  $m\mu$  using distilled water as the blank. After reading, add one drop of neutralized sodium cyanide to both unknown and blank.

Mix, let stand 2 minutes, and read again at 635  $m\mu$ , setting the absorbance at 0 with the blank. Reading is  $D_2$ .

$$F_m = \frac{\text{Hgb., g. per 100 ml.}}{D_1 - D_2}$$

## TOTAL NONPROTEIN NITROGEN (N.P.N.)

(Whole Blood)

**Reagents. Digestion Mixture.**—Prepare selenium dioxide from selenium by heating selenium to dryness in an evaporating dish with a 1:1 mixture of nitric acid and distilled water. When dry, add water and heat to dryness again. Continue additions of acid and evaporations until only the white crystals of  $\text{SeO}_2$  are present, with no trace of free selenium (black color). Protect  $\text{SeO}_2$  from moisture or it will turn pink. If this happens, add a little dilute nitric acid and again evaporate to dryness. Dissolve 1 g. of copper sulfate and 1 g. of selenium dioxide in distilled water. Dilute to 50 ml. with water. Add 150 ml. of concentrated sulfuric acid and 50 ml. of 85% phosphoric acid. For use, dilute about 150 ml. of the acid mixture with 100 ml. of distilled water. The diluted reagent must be balanced against previously titrated Nessler's reagent. Ten milliliters of a 1:10 dilution should be neutralized by 9 to 9.3 ml. of Nessler's reagent, with phenolphthalein being used as an indicator. Adjust the digestion mixture by addition of undiluted acid mixture or water as necessary.

**Mercuric Potassium Iodide Solution (Nessler's Stock Solution).**—Transfer to a Florence flask 150 g. of potassium iodide and 100 g. of iodine. Add 100 ml. of water and 140 to 150 g. of metallic mercury. Shake the flask continuously and vigorously for from 7 to 15 minutes, or until nearly all of the dissolved iodine has disappeared. The solution will become hot. When the red solution of iodine becomes visibly pale, cool in running water and continue the shaking until the red color of the iodine has been replaced by the greenish-yellow color of the double iodide. Do not cool the solution too soon. Separate the solution from the surplus mercury by decantation and by washing with liberal quantities of distilled water. Dilute the solution and washings to a volume of 2 liters.

**Nessler's Working Solution.**—To 1400 ml. of 10% sodium hydroxide add 300 ml. of mercuric potassium iodide solution and 300 ml. of distilled water. Mix. Nessler's solution must be titrated against 1 *N* hydrochloric acid using phenolphthalein as an indicator: 20 ml. of 1 *N* hydrochloric acid should be neutralized by 11 to 11.5 ml. of Nessler's reagent. If the Nessler's reagent is too alkaline (i.e., less than 11 ml. when used in the titration), water can be added to the solution to adjust it to the proper pH.

**Gum Ghatti Solution.**—Place 20 g. of gum ghatti on a copper screen and suspend in a 1000-ml. cylinder of distilled water just below the surface of the water. Allow to stand 18 to 24 hours. Remove screen and filter through a towel. Add 1 g. of mercuric chloride. Keep in refrigerator.

**Standard Ammonium Sulfate Solution.**—Ammonium sulfate, c.p., special pyridine-free, should be dried more than one-half hour at 110°C. and then allowed to cool for 20 minutes in a desiccator. Weigh on an analytical balance 0.4716 g. Wash into a beaker to dissolve. Then wash into a liter volumetric flask. Add 1 ml. concentrated, c.p. hydrochloric acid and dilute to mark with distilled water. Keep in a well-stoppered bottle. One milliliter equals 0.1 mg. of nitrogen.

**Procedure.**—Prepare protein-free filtrate by adding 1 volume of blood or serum to 7 volumes of water; then add 1 volume of 0.66 *N*  $\text{H}_2\text{SO}_4$ , mix, and allow to turn

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dark brown; finally, add 1 volume of 10% (wt./vol.) sodium tungstate, mix, allow to stand 2 minutes, and filter. Transfer 5 ml. of protein-free filtrate to a Pyrex tube graduated at 35 and 50 ml. (N.P.N. tube). Add 1 ml. of digestion mixture and 3 or 4 glass beads. Boil vigorously over a microburner until mixture turns brown and fumes appear. Boil until color disappears. Remove from flame and cool to room temperature. Add a few milliliters of distilled water. Add 1 ml. of gum ghatti. Dilute to the 35-ml. mark on tube with distilled water. Mix. Prepare a blank as follows: Place 1 ml. of digestion mixture in an N.P.N. tube; add 1 ml. of gum ghatti, and dilute to the 35-ml. mark with water and mix. Add to the unknown and blank, 15 ml. of Nessler's solution. Add quickly by blowing the Nessler's solution into the center of the mixture in the tube. Insert rubber stopper and mix. Let stand 10 minutes after Nesslerization. Centrifuge unknown and blank for 2 minutes. Read in a spectrophotometer at a wavelength of 480  $m\mu$  in cuvetts (19 by 150 mm.).

Repeat if test is cloudy after centrifuging. (Cloudiness may be due to improperly prepared solutions, especially an improper amount of alkali in Nessler's solution.) Repeat if a yellow or orange precipitate results after centrifuging. The precipitate should be colorless. An excess of tungstic or sulfuric acid will cause a yellow precipitate during digestion. Nessler's reagent should be added quickly without allowing it to run down the sides of the tube. The contents of the tube should be mixed first before Nesslerization.

**Calculations.**—Obtain N.P.N. values in mg. per 100 ml. from calibration curve. If nonprotein nitrogen reads above 60 mg. per 100 ml., repeat on filtrate aliquots of 2 ml. or 1 ml. and multiply results by appropriate factors (2.5 if 2 ml. are used, 5 if 1 ml. is used).

**Calibration Curve.**—Place 1 ml. (20 mg. per 100 ml.), 1.5 ml. (30 mg. per 100 ml.), 2 ml. (40 mg. per 100 ml.), and 3 ml. (60 mg. per 100 ml.) of ammonium sulfate standard solution in each of 4 N.P.N. tubes. Add 1 ml. of digestion mixture to each. Add 1 ml. of gum ghatti to each. Dilute to the 35-ml. mark with distilled water. Mix.

Prepare a blank as follows: Place 1 ml. of digestion mixture in an N.P.N. tube; add 1 ml. of gum ghatti; dilute to the 35-ml. mark with water and mix. Blow 15 ml. of Nessler's solution into each mixture. Mix well and let stand 10 minutes. Read each dilution within 20 minutes after Nesslerization in the spectrophotometer, using cuvetts (19 by 150 mm.) and a wavelength of 480  $m\mu$ , with the blank set at 100 per cent transmittance. Repeat several times on new dilutions, and plot average readings on semilogarithmic paper against corresponding values in mg. per 100 ml. of nonprotein nitrogen.

**NOTES.**—Normal values: 25 to 40 mg. per 100 ml. of blood. In normal blood the N.P.N. of the cells is about 50% higher than in plasma, but in retention the two approximate. Whole blood should be used in the determination. Blood obtained after a meal will give results 5 to 10 mg. higher than fasting blood. N.P.N. includes all nitrogen left after precipitation of protein constituents of the blood. It includes urea, uric acid, creatinine, ammonia, amino acids, and other nitrogenous substances ("rest N").

### BLOOD pH (Whole Blood)

The Metrohm blood electrode is suited to measure the pH of blood, by pressing the blood directly from a syringe or sucking directly from a vacuum tube into the electrode. A water jacket permits connection to a circulating thermostat. The liquid to be measured reaches the measuring temperature of 37°C. within a

few seconds. The electrode is suited for the pH range 1 to 9 at temperatures varying from  $+15^{\circ}$  to  $+55^{\circ}\text{C}$ . The minimum volume of liquid required is 0.5 ml.

In the following paragraphs are listed certain precautions. These precautions must be stringently adhered to in order that the procedure may be followed with ease and accuracy.

The procedure used in the drawing of the blood sample is of great importance. Ideally there is no substitute for arterial blood. For routine evaluation of all clinical problems, venous blood, when drawn properly, is extremely useful. The tourniquet is applied lightly, the patient is instructed NOT to flex or squeeze the fingers; and the venous blood is obtained with a vacuum blood tube containing heparin. The pH value should be measured within one-half hour. The pH of whole blood will change approximately 0.01 pH units every 10 minutes at  $37^{\circ}\text{C}$ . At  $27^{\circ}\text{C}$ . the change is approximately 0.005 pH units every 10 minutes. If the pH cannot be measured within one-half hour, the blood should be kept in ice water. Under these circumstances, the blood will keep as long as 4 hours.

Mineral oil should never be used. All electrodes should be thoroughly rinsed with physiological saline after each blood pH measurement. After completing a series of measurements, the electrode should be washed with a detergent such as 1% Alconox or Triton X-100. Cleanliness is of greatest importance. Platelet clumps can be avoided by taking the sample below the surface of the blood and away from the walls of the blood tubes.

For the most precise work and for all pulmonary function work, pH should be measured at the subject's body temperature. However, for routine clinical screening, the use of a fixed temperature between  $37^{\circ}\text{C}$ . and  $38^{\circ}\text{C}$ . for all samples is satisfactory. The meter and the circulating thermostat must be connected together to a true ground. The tip of the reference electrode should be covered and the side plugged when not in use. The glass electrode should never be allowed to dry out. Keep filled with physiologic saline between determinations.

**Reagents.** Standard Acetate Buffer—pH 4.165 at  $37^{\circ}\text{C}$ .

PNP Buffer—pH 6.975 at  $37^{\circ}\text{C}$ . (0.04 M *p*-nitrophenol and 0.40 M sodium *p*-nitrophenolate).

**Procedure.**—The instrument consists of a combination of Haake's thermostat type "F" water bath, a Metrohm Blood Measuring Chain EA 520, and an expanded scale pH meter.

Turn on water bath and allow to come to body temperature, which requires 5 to 10 minutes. Beaker EA 753 is filled with gel type KCl solution. The reference electrode is filled above the mercury with saturated solution of KCl and is left unplugged during the measurements.

With the stopcock in position 1, an appropriate buffer near the usual pH of blood is drawn into the electrode until the liquid is seen above the electrode chamber. The position of the stopcock is then changed to 2. The capillary electrode is lifted and placed in intermediate vessel EA-753. The pH meter is ad-



(1)



(2)



(3)

justed against the standard buffer. The tip of the electrode is lifted from the intermediate vessel. With the stopcock in position 3, physiological saline is passed through the electrode to rinse it out by closing the hole on top of the rinsing bottle with the finger and squeezing the bottle. With the stopcock in

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position 1, the tip of the electrode is placed below the surface of the blood in the blood tube and a sample of blood is drawn to the same level as the previous buffer. The stopcock is then turned to position 2. The capillary electrode is lifted and placed so that the tip of the electrode is in intermediate vessel EA 753. The tip of the reference electrode should be checked to see if it is in place in the intermediate vessel EA 753. A reading is then taken. This reading should follow within 1 minute the reading of the buffer. The capillary electrode is lifted and placed so that the tip of the electrode is out of the intermediate vessel. The electrode is rinsed, as above, with physiological saline from the rinse bottle. The electrode is cleaned by applying a squeeze bottle containing 1% solution of Triton X-100 to the outlet tube and squeezing a small quantity of this solution through the electrode. The electrode is again rinsed with physiological saline and then filled with the same solution. The instrument is ready for next determination.

NOTE.—Normal values: 7.36 to 7.40.

### ALKALINE AND ACID PHOSPHATASE

(Serum)

**Reagents.** Stock Phenol Reagent.—Dissolve 100 g. of sodium tungstate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) and 25 g. of sodium molybdate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) in 700 ml. of water in a 1500-ml. round-bottomed flask. Add 50 ml. of 85% phosphoric acid and 100 ml. of concentrated hydrochloric acid. Mix thoroughly. Fit a reflux condenser to the flask by means of a rubber stopper or cork wrapped in tin foil, or, preferably, use standard-taper all-glass joints. Boil the solution gently for 10 hours. Remove the condenser, add 150 g. of lithium sulfate ( $\text{Li}_2\text{SO}_4$ ), and wash down with 50 ml. of water. After solution is complete, add 5 to 10 drops of liquid bromine, and boil for 15 minutes to remove the excess bromine. The solution should be clear and golden yellow in appearance. If it shows a greenish tint, repeat the treatment with bromine. Cool the solution to room temperature, dilute to 1 liter, and filter if necessary through glass wool into a glass-stoppered brown bottle. This reagent is stable for several months.

**Dilute Phenol Reagent.**—Dilute 1 volume of stock phenol reagent with 2 volumes of distilled water. This solution is reasonably stable when stored in a dark-brown bottle. Discard when a greenish tint becomes noticeable.

**Substrate:** 0.01 *M* Disodium Phenyl Phosphate.—Dissolve 2.18 g. of reagent grade disodium monophenyl phosphate in 1 liter of distilled water. Sterilize the solution by bringing it quickly to the boiling point. Then cool it immediately, add a few drops of chloroform, and store in the refrigerator.

**Alkaline Buffer:** 0.06 *M*  $\text{Na}_2\text{CO}_3$ , 0.04 *M*  $\text{NaHCO}_3$ .—Dissolve 6.36 g. of anhydrous sodium carbonate and 3.36 g. of sodium bicarbonate in approximately 500 ml. of distilled water contained in a 1-liter volumetric flask. Dilute to mark and mix. Store in a refrigerator. The pH of this solution should be 10.0.

**Acid Buffer:** 0.176 *M* Disodium Citrate, 0.024 *M* Monosodium Citrate.—Dissolve 21.0 g. of reagent grade citric acid monohydrate, crystalline, in 200 ml. of distilled water contained in a 500-ml. volumetric flask. Add 188 ml. of standardized 1 *N* sodium hydroxide, and dilute to volume. The pH of this solution should be 4.9. Check potentiometrically and adjust if necessary by the addition of either 0.1 *N* sodium hydroxide or 0.1 *N* hydrochloric acid. Add a few drops of chloroform and store in the refrigerator.

**Buffered Alkaline Substrate.**—Mix 500 ml. of disodium phenyl phosphate with 500 ml. of alkaline buffer. Store in refrigerator.

**Buffered Acid Substrate.**—Mix 250 ml. of disodium phenyl phosphate with 250 ml. of acid buffer. Store in refrigerator.

**Phenol Stock Standard, 1 mg. per ml.**—Transfer approximately 1.2 g. of reagent grade crystalline phenol to a 1-liter volumetric flask and dissolve in approximately 200 ml. of 0.1 *N* hydrochloric acid. Dilute to volume with 0.1 *N* hydrochloric acid.

**Standardization.**—Standardize by titration 0.1 *N* solutions of sodium thiosulfate (25.0 g. of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  per liter) and of iodine (prepared by diluting a solution containing 25 g. of pure KI, 25 ml. of water, and 12.7 g. of resublimed iodine to 1 liter). The 0.1 *N* solution of potassium biiodate (3.250 g. of reagent grade  $\text{KH}(\text{IO}_3)_2$  per liter) is used to standardize the 0.1 *N* thiosulfate. Then the thiosulfate is used to standardize the 0.1 *N* iodine solution.

Immediately prior to titration of biiodate with thiosulfate, iodine is liberated from the standard solution by transferring 25 ml. to a solution prepared by adding 5 ml. of 6 *N* hydrochloric acid to a solution of 2 g. of pure potassium iodide in 3 ml. of water.

To standardize the phenol stock solution, accurately transfer 25 ml. of the solution to a 250-ml. glass-stoppered Erlenmeyer flask, add 50 ml. of 0.1 *N* sodium hydroxide solution (4.0 g. per liter) and heat to 65°C. Add 25 ml. of 0.1 *N* iodine and mix. Stopper the flask and allow to stand at room temperature for 45 minutes. Add 5 ml. of concentrated hydrochloric acid, and titrate the excess iodine with 0.1 *N* sodium thiosulfate, using 1 ml. of 1% starch as indicator.

**Calculation.**—

$$\text{Mg. phenol per 25 ml.} = 1.568 \times (\text{ml. 0.1 } N \text{ I}_2 - \text{ml. 0.1 } N \text{ Na}_2\text{S}_2\text{O}_3 \text{ used})$$

If more than 25 mg. of phenol is found in 25 ml., adjust to this concentration by suitable dilution with 0.1 *N* hydrochloric acid. This solution keeps indefinitely at refrigerator temperature.

**Dilute Phenol Standard, 0.05 mg. per ml.**—Transfer 5 ml. of the phenol stock standard to a 100-ml. volumetric flask, and dilute to volume with distilled water. Store in refrigerator. This solution may be kept one month.

**Procedure. Alkaline Phosphatase.**—Transfer 4 ml. of buffered alkaline substrate to each of two test tubes (5 by 5/8 in.) labeled A and B and allow the solutions to warm for 3 minutes in a water bath regulated at 37°C. Add 0.2 ml. of serum (or plasma) to tube A, mix at once and allow both tubes to remain in the water bath. Exactly 15 minutes after the addition of serum to tube A, pipet 2 ml. of dilute phenol reagent into each tube, and mix well. Add 0.2 ml. of serum to tube B, mix again, and centrifuge both tubes.

To prepare the standard, measure 1 ml. of dilute phenol standard into a test tube. Add 3.2 ml. of distilled water and 2 ml. of dilute phenol reagent and mix.

To prepare the reagent blank, add 2 ml. of dilute phenol reagent to a tube containing 4 ml. of distilled water and mix.

Add 2 ml. of clear supernatant solution, 2 ml. of prepared standard, and 2 ml. of reagent blank to appropriately labeled tubes. To each tube add 8 ml. of 6% sodium carbonate, mix well, and allow to stand 20 minutes for complete color development.

Measure the resulting blue colors in a suitable spectrophotometer at 660  $m\mu$



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(red). With instruments calibrated in terms of absorbance (optical density) pour the reagent blank into a suitable cuvet, and adjust absorbance reading to zero against this solution. Record readings of the standard and of solutions A and B. Subtract reading of solution B from that of solution A.

**Calculation.**—

$$\text{K.A.U. per 100 ml.} = 0.0161 \times \frac{R_a - R_b}{R_s} \times \frac{6.2}{2.0} \times \frac{100}{0.2}$$

$$\text{K.A.U. per 100 ml.} = 25.0 \times \frac{R_a - R_b}{R_s}$$

where K.A.U. = alkaline phosphatase expressed as King-Armstrong Units

0.0161 = milligrams of phenol in final standard solution

$R_a$  = absorbance reading of solution A

$R_b$  = absorbance reading of solution B

$R_s$  = absorbance reading of phenol standard

6.2 = combined volume of serum plus buffered substrate plus dilute phenol reagent

2.0 = aliquot portions of this solution taken for color development

0.2 = volume of serum taken for analysis

**Acid Phosphatase.**—Transfer 4 ml. of buffered acid substrate to each of two test tubes, labeled C and D, and warm the solutions for 3 minutes in a water bath at 37°C. Add 0.2 ml. of unhemolyzed serum or plasma to tube C, mix at once, and allow both tubes to remain in the water bath. Exactly 1 hour after the addition of serum to tube C, pipet 2 ml. of dilute phenol reagent into each tube, and mix well. Add 0.2 ml. of serum to tube D, mix again, and centrifuge both tubes.

To prepare the treated standard (standard plus phenol reagent), measure 1 ml. of dilute phenol standard into a test tube. Add 3.2 ml. of distilled water and 2 ml. of dilute phenol reagent and mix.

To prepare the reagent blank, add 2 ml. of dilute phenol reagent to a tube containing 4.2 ml. of distilled water, and mix. (When both alkaline and acid phosphatase are to be determined, only one standard and reagent blank need be prepared.)

Add 4 ml. of each clear supernatant solution, prepared standard, and reagent blank to an appropriately labeled tube. To each solution add 6 ml. of 8% sodium carbonate, mix well, and allow to stand for 20 minutes.

Pour the reagent blank into a suitable cuvet and set the indicator of the spectrophotometer to zero absorbance against this solution at 660  $m\mu$  (red). Record absorbance reading of the standard and of solutions C and D. Subtract reading of solution D from that of solution C.

**Calculation.**—

$$\text{K.A.U. per 100 ml.} = 0.0322 \times \frac{R_c - R_d}{R_s} \times \frac{6.2}{4.0} \times \frac{100}{0.2}$$

$$\text{K.A.U. per 100 ml.} = 25.0 \times \frac{R_c - R_d}{R_s}$$

where K.A.U. = acid phosphatase expressed as King-Armstrong Units

0.0322 = milligrams of phenol in final standard solution

$R_c$  = absorbance reading of solution C

$R_d$  = absorbance reading of solution D

$R_s$  = absorbance reading of phenol standard

6.2 = combined volume of serum plus buffered substrate plus dilute phenol reagent

4.0 = aliquot portion of this solution taken for color development

0.2 = volume of serum taken for analysis

NOTES.—Normal values:

1. Alkaline phosphatase: adults 4 to 10 K.A.U., children 10 to 20 K.A.U.

2. Acid phosphatase, 0–4 K.A.U.

The range of alkaline phosphatase values which can be determined by this procedure includes 0 to 70 units. If higher levels are found (i.e., absorbance  $> 1$ ), an accurate value may be obtained by diluting 1 volume of the final solution with 1 or 2 volumes of distilled water before measuring its absorbance. Multiplication by the dilution factor gives the factor to be used for these calculations.

Acid phosphatase values of 0 to 30 units can be determined by this procedure. Higher values may be determined also by dilution of the blue complex with distilled water before reading.

Hemolyzed specimens of serum (plasma) should not be used for acid phosphatase determinations. Erythrocytes are known to contain large amounts of an acid phosphatase with optimal activity at pH 6. Results may, therefore, be vitiated even by slight hemolysis.

Only very pure disodium phenyl phosphate, phenol-free, is suitable for use as substrate.

## INORGANIC PHOSPHORUS

(Serum and Urine)

**Reagents. Molybdate II Reagent.**—Dissolve 25 g. of c.p. ammonium molybdate in 300 ml. of 10 *N* sulfuric acid. Dilute to 1 liter with distilled water (2.5% ammonium molybdate in 3 *N* sulfuric acid).

**Elon (*p*-Methylaminophenol Sulfate, Eastman Kodak, Practical No. P615) Stock Solution.**—Dissolve 3 g. of c.p. sodium bisulphite in 100 ml. of distilled water. Add 1 g. of Elon. Shake well. Store in brown bottle in the refrigerator.

**Elon Dilute Working Solution.**—Dilute 10 ml. of Elon stock solution to 100 ml. with distilled water. Mix well. Prepare fresh on the day of use.

**Phosphorus Stock Standard Solution.**—Dissolve 0.3514 g. of pure, well-dried monopotassium phosphate in 10 ml. of 10 *N* sulfuric acid. Dilute to 1 liter in a volumetric flask (1 ml. = 0.8 mg. phosphorus).

**Phosphorus Working Standard.**—Transfer 25 ml. of stock standard solution to a 500-ml. volumetric flask. Dilute to mark with 5% trichloroacetic acid (5 ml. = 0.02 mg. P represents 4 mg. per 100 ml. phosphorus).

**Procedure. Serum.**—Place 9.0 ml. of 10% (wt./vol.) trichloroacetic acid in a conical centrifuge tube. Add 1.0 ml. of serum. Mix thoroughly. Allow to stand 5 to 10 minutes. Centrifuge until clear. Pipet 5.0 ml. of supernatant fluid into a clean, acid-washed test tube. Prepare a blank by pipetting 5.0 ml. of 5% trichloroacetic acid into a similar tube. Prepare a standard by pipetting 5.0 ml. of the working standard (5 ml. = 0.02 mg. P) into another tube. Add 1.0 ml. of molybdate II to each tube. Mix well. Add 4.0 ml. of dilute Elon to each tube.

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Mix, in succession, immediately after the addition to each tube. Allow to stand 10 minutes. Read absorbance of the unknown and of the standard in the spectrophotometer after 10 minutes (and before 60 minutes) at  $680\text{ m}\mu$  against the reagent blank set at 100% *T* (zero absorbance). Use clean, dry cuvetts (12 by 75 mm.). Obtain serum phosphorus value by using formula 1 under calculations below.

**NOTE.**—The blood specimen must be drawn while the patient is fasting. It is necessary that the determination be carried out on fresh, unhemolyzed serum separated as soon as possible from the red cells because of the ease of hydrolysis of phosphate esters in the red cells by the phosphatases in the serum. Both hemolysis and prolonged standing of the blood specimen will increase the phosphorus level. The serum should be refrigerated for a short time if delayed analysis is unavoidable.

**Urine.**—Dilute 1.0 ml. of urine (a measured 24-hour specimen) to 50 ml. with 5% trichloroacetic acid in a 50-ml. glass-stoppered volumetric flask. Mix well and filter, if not perfectly clear, through No. 40 Whatman filter paper. Add 5.0 ml. of diluted urine to a clean, acid washed test tube. Prepare a blank and standard as under method for serum above. Add 1.0 ml. of molybdate II reagent to each tube. Mix well. Add 4.0 ml. of dilute Elon and mix each tube immediately. Allow to stand at least 10 minutes. Read absorbance of the unknown and of the standard in the spectrophotometer at  $680\text{ m}\mu$  against the reagent blank set at 100% *T* (zero absorbance). Report results in grams of phosphorus excreted in 24 hours. Obtain value by using formula 2 under calculations below.

**Calculations.**—

### 1. Serum:

Absorbance of unknown  $\times \frac{\text{conc. of std.}}{\text{absorbance of std.}} = \text{mg. per 100 ml. serum inorganic phosphorus}$

### 2. Urine:

Absorbance of unknown  $\times \frac{\text{conc. of std.}}{\text{absorbance of std.}} \times 5 \times \frac{\text{ml. per 24 hr. spec.}}{1000} = \text{g. P per 24 hr.}$

**NOTES.**—Normal values. Adults, 3 to 4.5 mg. per 100 ml. (serum)  
Children, 4 to 6 mg. per 100 ml. (serum)  
Approx. 1.0 g. per 24 hours (urine)

## PREGNANEDIOL

(Urine)

**Procedure.**—The entire 24-hour collection of urine is introduced into a suitable flask fitted with a reflux condenser together with 0.1 of its volume of concentrated hydrochloric acid and 200 ml. of toluene. The mixture is heated to boiling, the boiling continued for 15 minutes, and then cooled rapidly in running water.

The mixture is transferred to a suitable separatory funnel. The toluene is separated and the aqueous fraction extracted with two further quantities of 200 ml. of toluene. The combined toluene extracts are washed twice with two 100-ml. quantities of 10% sodium hydroxide and twice with 100-ml. quantities of water. The toluene extract is evaporated down to dryness in a 500-ml. flask attached to a vacuum still. It is essential to have the flask heated by a water bath and to begin heating from the cold; otherwise trouble from "bumping" may be encountered.

The dry residue is dissolved in 10 ml. of absolute alcohol, the solution being

transferred to a 100-ml. conical flask, and 40 ml. of hot (about 70°C.) 0.1 *N* sodium hydroxide solution is added to the alcoholic solution. (This process can be used to transfer completely the contents of the 500-ml. flask into the 100-ml. conical flask.) The mixture is allowed to cool to room temperature, after which the flask is placed in a refrigerator (5°C.) overnight. The contents of the flask are filtered through a No. 42 Whatman filter paper. The residue is washed with 40 ml. of cold water (5°C.). (The cold water should be transferred from the original conical flask.) The filter paper containing the residue is put back into the original conical flask and 10 ml. of absolute alcohol are added. When the solution of pregnanediol has been effected, 40 ml. of hot water (about 70°C.) are added. The mixture is allowed to cool to room temperature after which it is placed in a refrigerator (5°C.) overnight. The contents of the flask are then filtered through a No. 42 Whatman filter paper. The residue is washed with 40 ml. of cold water (5°C.). The residue on the filter paper is dissolved in about 40 ml. of absolute alcohol (contained in the original conical flask), the filtrate being collected in a weighed 50-ml. beaker. The alcohol is evaporated off in a hot oven maintained at 100°C. The dry beaker is allowed to cool in a desiccator. The increase of weight represents pregnanediol separated.

NOTES.—In extensive investigation, it has been found that the excretion of pregnanediol by the male is less than 1 mg. per day, and in the female during the reproductive phase of life, the maximum is 4.5 to 6.5 mg. per day. In late pregnancy it has been found that pregnanediol as determined by this method agrees very closely with the content of non-ketonic alcohols in the neutral steroid fraction.

## TOTAL PROTEINS

(Serum and Spinal Fluid)

**Reagents. Biuret Reagent.**—Dissolve 45 g. sodium potassium tartrate in approximately 400 ml. of 0.2 *N* NaOH (carbonate-free), add 15 g. copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) and dissolve *completely* with stirring. Add 5 g. potassium iodide and make up to the mark in a liter volumetric flask with 0.2 *N* NaOH.

**Protein Standard.**—A commercially standardized preparation of freeze-dried pooled human serum is used to prepare a series of known protein solutions covering the desired range of concentrations to be used in plotting a calibration curve for the spectrophotometer. The protein value is indicated on the package insert and is ready for use on the addition of distilled water. These known standard dilutions are processed by the technique outlined below and read in a spectrophotometer at 450  $m\mu$ , using cuvetts with a 1-cm. light path. The transmittance readings are plotted against the corresponding dilutions on semilogarithmic paper. The curve should be checked frequently against a known protein solution.

**Procedure. Serum.**—Measure 0.1 ml. serum into a test tube containing 4.9 ml. of 0.85% sodium chloride solution. Add 5 ml. of biuret reagent. Mix well and let stand approximately 30 minutes in a water bath at 30° to 32°C. Read in a spectrophotometer at 555  $m\mu$  using a reference blank made at the same time containing 5 ml. of 0.85% sodium chloride solution and 5 ml. of biuret reagent. Obtain the values from the calibration curve below.

**Calibration Curve. Protein Standards.**—*a.* 180 mg. protein per 100 ml. (9 g. protein per 100 ml. based on use of a 0.1-ml. sample of serum and a volume of 10 ml.): Use clear, pooled human or animal serum and determine total protein content by macro- or micro-Kjeldahl technique. Knowing the protein content,

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measure into a 250-ml. volumetric flask a quantity of pooled serum containing 0.45 g. of protein. Make up to 250-ml. mark with 0.85% sodium chloride.

*b.* 140 mg. protein per 100 ml. (7 g. protein per 100 ml. based on the use of 0.1-ml. sample of serum and a total volume of 10 ml.): Proceed exactly as above except measure into the 250-ml. volumetric flask a volume of serum containing 0.35 g. protein.

*c.* 80 mg. protein per 100 ml. (4 g. per 100 ml.): Proceed as above except measure into the 250-ml. volumetric flask a volume of serum containing 0.2 g. protein.

Use 5 ml. of each dilution and 5 ml. of biuret reagent. Allow to stand in a water bath at 30° to 32°C. for 30 minutes and read transmittance of each as soon as possible in a spectrophotometer at 555 m $\mu$  or in a photometer with round cups and green filter. For spectrophotometer readings prepare a reference blank by adding 5 ml. of biuret reagent to 5 ml. of 0.85% sodium chloride and incubate with test. Repeat several times on new dilutions so that an average of the transmittance readings will make a straight line when plotted on semilogarithmic graph paper against the protein values in g. per 100 ml.

NOTE.—Normal values: 6 to 8 g. per 100 ml. (total protein).

**Spinal Fluid.**—Centrifuge specimen for 10 minutes at 1500 r.p.m. Label a 5-in. test tube "T" (test), another "B" (blank), and a third tube "S" (standard). Prepare only one blank and one standard for a series of specimens to be analyzed. Place 1 ml. of centrifuged, clear, unhemolyzed spinal fluid in the tube marked "T." Place 1 ml. of standard and 1 ml. of distilled water in their appropriate tubes. Stopper each tube with a clean rubber stopper and mix by inversion. Add 3 ml. of 3% sulfosalicylic acid to each tube. Allow tubes to stand for 10 minutes. Mix again by inversion. Read in a spectrophotometer at 450 m $\mu$  (use cuvetts with a 1-cm. light path).

**Calculations.**—

$$\frac{\text{Absorbance of test}}{\text{Absorbance of standard}} \times \text{conc. of standard} = \text{mg. protein per 100 ml. spinal fluid}$$

NOTES.—Normal values: 20 to 40 mg. per 100 ml.

Methods designed for the analysis of serum proteins lack sensitivity when applied to the analysis of the small protein content of body fluids. In addition, urine and body fluid exudates contain chromogens and other materials which may affect the standard conditions used for analysis of serum protein. Specific methods for the analysis of body fluids include turbidimetric analysis by organic acids (trichloroacetic acid, sulfosalicylic), the measurement of specific amino acid content by Folin Cialteau reagent, or various dye techniques.

The method outlined here utilizes sulfosalicylic acid which precipitates protein in fine clumps, the turbidity of which is proportional within a limited range to protein concentration. The turbidity produced by albumin is about twice that for globulin. Albumin is the predominant protein in spinal fluid and all other body fluids.

### ALBUMIN AND ALPHA, BETA, AND GAMMA GLOBULINS (Serum)

**Reagents.** Stock Phosphate Solution: 3.33 M, pH 6.5.—Add 2268 g. of potassium phosphate, monobasic ("Sorensen's potassium phosphate"—KH<sub>2</sub>PO<sub>4</sub>) to about 4000 ml. of solution containing 335 g. of sodium hydroxide. Shake or stir until

completely dissolved, cool to room temperature, then dilute to 5000 ml. or add water until the final weight of the solution is 6675 g.

**Dilute Phosphate Solutions.**—1. Weigh 1235 g. of stock phosphate solution into a 1000-ml. volumetric flask. Dilute to the mark with distilled water.

2. Weigh 1000 g. of stock phosphate solution into a 1000-ml. volumetric flask. Dilute to the mark with distilled water.

3. Weigh 785 g. of stock phosphate solution into a 1000-ml. volumetric flask. Dilute to the mark with distilled water.

4. Weigh 625 g. of stock phosphate solution into a 1000-ml. volumetric flask. Dilute to the mark with distilled water.

**Procedure.**—Set up five colorimeter tubes marked B (blank), 1, 2, 3, and 4. Into tube B measure 10 ml. of distilled water and into the other tubes measure 10 ml. of the corresponding numbered dilute phosphate solution. Now measure 1 ml. of serum and 1.5 ml. of water into a small test tube. Add 7.5 ml. of stock phosphate solution, allowing it to flow directly into the diluted serum. Invert the tube five or six times to mix, then transfer 1 ml. of the mixture to each of the previously prepared colorimeter tubes, again allowing the serum-phosphate mixture to flow directly into the solution in the colorimeter tubes. Mix the contents of each tube thoroughly by rotating or inverting the tube, but avoid vigorous shaking. Allow to stand for about 15 minutes, then measure the absorbance of tubes 1, 2, 3, and 4 at 650  $m\mu$ , using tube B to set the spectrophotometer at 0 absorbance (100%  $T$ ).

**Calculations.**—Absorbance of tube number 1 times  $F$  equals total protein. Absorbance of tube number 1 minus the absorbance of tube number 2 times  $F$  equals albumin. Absorbance of tube number 2 minus the absorbance of tube number 3 times  $F$  equals alpha globulin. Absorbance of tube number 3 minus the absorbance of tube number 4 times  $F$  equals beta globulin. Absorbance of tube number 4 times  $F$  equals gamma globulin.

**Calibration.**—The factor  $F$  used in the above calculations must be determined for the particular type of spectrophotometer used. Obtain a sample of clear, normal human serum. Determine the total protein content of this serum by any accurate, convenient method. Carry the serum through the previously given procedure, using the blank and tube number 1 only (in triplicate). Divide the total protein of the serum by the average optical density of tube number 1 to give factor  $F$ .

## SALICYLATE

(Serum, Plasma, Whole Blood)

**Reagents.** Isotonic Sodium Sulfate (2%  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ).

1.5%  $p$ -Nitraniline in 5  $N$  Hydrochloric Acid.

**Standard Salicylate Solution** (50 mg. sodium salicylate dissolved in 100 ml. water). Store in the refrigerator.

**Procedure.**—Serum, plasma, or whole blood, 0.2 ml. is mixed with 6.6 ml. of isotonic sodium sulfate. Then 0.6 ml. of 10% (wt./vol.) zinc sulfate solution followed by 0.6 ml. of 0.5  $N$  sodium hydroxide are added to precipitate the proteins, and the mixture is filtered. A Whatman No. 1 paper is suitable. A standard and a reagent blank are carried through simultaneously with the unknown by substituting 0.2 ml. of salicylate solution and 0.2 ml. of isotonic sodium sulfate for the blood, and 4 ml. of filtrate are mixed with 0.8 ml. of  $p$ -nitraniline solution. The solu-

tion is chilled in ice water. Sodium nitrite solution (10% wt./vol.), 0.6 ml., is added, and, after standing in ice water for 2 to 3 minutes, the solution is made alkaline by adding 1.2 ml. of 4 *N* sodium hydroxide. The colors develop immediately and are stable for a considerable time. They can be measured in a spectrophotometer at a 500-m $\mu$  setting.

Calculation.—

$$\text{Conc. unknown} = \frac{\text{absorbance unknown}}{\text{absorbance standard}} \times \text{conc. standard}$$

NOTE—Therapeutic level is 30 to 45 mg. per 100 ml.

Since only small traces of salicylates are present in the red cells, whole blood levels are lower than the corresponding plasma levels. The former, however, can be converted to the latter, to a close approximation, by the use of the equation:

$$P = \frac{B}{100 - H}$$

where *P* and *B* are the plasma and whole blood levels in milligrams per 100 ml. and *H* is the hematocrit.

## SODIUM AND POTASSIUM

(Serum)

### SODIUM

**Reagents.** Uranyl Zinc Acetate Reagent.—*Solution A.* To 38.5 g. of reagent grade uranyl acetate are added about 200 ml. of distilled water and 7 ml. of glacial acetic acid. The acetate is dissolved by gently heating and stirring. The solution is then cooled and diluted to 250 ml. in a volumetric flask.

*Solution B.* To 115.4 g. of reagent grade zinc acetate are added about 200 ml. of distilled water and 3.5 ml. of glacial acetic acid. The acetate is dissolved by gently heating and stirring. The solution is then cooled and diluted to 250 ml. in a volumetric flask.

The two solutions (A and B) are heated in separate beakers to 80° or 90°C. While hot, the mixture is placed in an incubator at 37°C. for 48 hours and is occasionally shaken. Owing to sodium impurities in the reagents, a precipitate of uranyl zinc sodium acetate usually forms and settles out. If no precipitate appears, 0.2 g. of precipitated uranyl zinc sodium acetate, as below, is added to saturate the solution with this triple salt. The solution is kept in the incubator and remains good indefinitely.

About 1 hour before use, the solution is removed from the incubator and allowed to come to room temperature. The bottle is shaken and as much solution as is needed is filtered off immediately before use.

**Uranyl Zinc Sodium Acetate.**—A small amount of the triple salt may be prepared by adding 15 ml. of the uranyl zinc acetate reagent to 1 ml. of a 5% solution of reagent grade sodium chloride. Five milliliters of 95% alcohol is added in small portions. The mixture is filtered with suction in a Gooch crucible. The precipitate is washed four times with 5-ml. portions of 95% ethyl alcohol, followed by four washings with 5-ml. portions of ethyl ether. The salt is then dried in a desiccator, containing calcium chloride, for at least 1 hour. The dry salt will keep indefinitely.

**Alcohol Wash Solution.**—Ninety-five per cent ethyl alcohol is saturated with uranyl zinc sodium acetate. This solution is stored in the incubator at 37°C. About 1 hour before use, it is brought to room temperature and shaken occasionally. It is filtered just before use.

**Procedure.**—With each set of serum measurements, simultaneous measurements are made on standard salt solution and a reagent blank. All measurements are made in duplicate or triplicate. One milliliter of serum is placed in a 3-in. porcelain evaporating dish. One milliliter of 4 *N* H<sub>2</sub>SO<sub>4</sub> and one drop of 1.25% (wt./vol.) ferric sulfate solution are added to each dish. The dishes are placed on a steam bath (or a sand bath) until the mixture becomes a dark syrupy liquid (1 or 2 hours). The dishes are then placed in a cold electric furnace, gradually raising the temperature to 550° to 600°C. This heat is maintained for 1 hour or until ashing is completed. There will be a red discoloration in the salt solution owing to excess iron. The dishes are allowed to cool to room temperature and the ash is transferred quantitatively to a graduated 25-ml. centrifuge tube. Transfers are made by washing four to 5 times with 4-ml. portions of distilled water. The solution is diluted to the 25-ml. mark and mixed.

After centrifuging for 5 minutes at about 2500 r.p.m., 20 ml. of the supernatant fluid are placed in a 50-ml. Pyrex beaker and evaporated to dryness in a drying oven at 110°C. Porous glass Gooch filter crucibles of 15-ml. capacity<sup>1</sup> are placed in filter funnels over 500-ml. filter flasks. (It is advisable to have the crucibles thoroughly cleaned with HCl beforehand and rinsed with distilled water.) The Gooch crucibles are prepared by washing once with water, three times with 2 ml. of alcoholic wash solution saturated with uranyl zinc sodium acetate, and three times with 2 ml. of ether. Air is suctioned through the Gooch crucibles for 10 minutes, following which they are placed in the desiccator for approximately 20 minutes and weighed.

To the dried extract of the ashed serum, 10 ml. of freshly filtered uranyl zinc acetate are added. The solution is mixed and allowed to stand for 30 minutes in a vessel containing water at room temperature. The contents of the beaker are filtered through the previously weighed Gooch crucible. (The procedure of filtration must be carried out at approximately constant temperature in order to avoid changes in solubility of the uranyl zinc sodium acetate.) The beaker and precipitate are washed ten times with 2 ml. of freshly filtered alcohol wash solution. The precipitate in the Gooch crucible is then washed three times with 2 ml. of ether. Suction is continued until the precipitate is thoroughly dry. The filter and precipitate are placed in a desiccator containing calcium chloride. The precipitate is dried for at least one-half hour. The precipitate in the Gooch crucible is weighed on an analytical balance.

**Calculations.**—The precipitate of uranyl zinc sodium acetate contains 1.495% of sodium.

Wt. of precipitate in grams  $\times$  1869 = mg. Na per 100 ml. of serum.

Wt. of precipitate in grams  $\times$  813 = milliequivalents of Na per liter of serum.

Correction is made for the blanks.

**NOTE.**—Normal values: 135 to 142 milliequivalents per liter.

<sup>1</sup>A. H. Thomas Co., No. 4141-C are satisfactory.



## POTASSIUM

**Reagents. Tetraphenylboron Solution.**—Exactly 5 g. of sodium tetraphenylboron reagent are dissolved in 50 ml. of distilled water, and transferred to a 100-ml. volumetric flask. Ten milliliters of 0.1 N NaOH are added and the solution is diluted to the mark. The solution should be virtually clear—the development of turbidity results either from contamination with potassium or from deterioration of the tetraphenylboron reagent. The tetraphenylboron solution is stable for at least one week at room temperature.

**Alkaline EDTA Solution.**—Seven and one-half grams of ethylenediaminetetraacetic acid, disodium salt, are transferred to a 500-ml. volumetric flask. Forty-four milliliters of 1.0 N NaOH are added, and the solution is diluted to the mark with distilled water. This solution is stable for at least two weeks at room temperature.

**Formaldehyde Solution.**—Formalin (37% formaldehyde) is diluted 1:1 with distilled water.

**Mixed Alkaline EDTA-Formaldehyde Solution.**—This solution is prepared fresh by mixing 2 parts of alkaline EDTA solution with 1 part of formaldehyde solution.

**Gum Ghatti Solution.**—Ten grams of gum ghatti tears are placed in a bag made of a double layer of gauze. The bag is suspended in a beaker containing 400 ml. of distilled water, upper surface of the water just covering the contents of the bag. After leaving it overnight, the bag is removed and discarded. The solution is mixed, allowed to stand for several hours, and then decanted and, if necessary, filtered.

**Potassium Standard Stock Solution.**—Into a 1-liter volumetric flask, 0.3728 g. of fused potassium chloride is carefully transferred and diluted to the mark with distilled water. The resultant stock solution contains 5 milliequivalents of potassium per liter.

**Potassium Standard Working Solutions.**—Zero-, 2-, 4-, 6-, 8-, and 10-ml. samples of the potassium standard stock solution are transferred to 50-ml. volumetric flasks. Twenty-five milliliters of the 8% trichloroacetic acid solution are added to each flask and the contents are diluted to the mark with distilled water. When employed as outlined in the procedure, these standards correspond to concentrations of serum potassium of 0, 2, 4, 6, 8, and 10 milliequivalents per liter, respectively, and these standards are used in constructing the calibration curve.

**Procedure.**—Trichloroacetic acid filtrates of serum are prepared by adding 5 ml. of 8% trichloroacetic acid solution to 1 ml. of serum in a 10-ml. volumetric flask or calibrated tube. The contents are diluted to the mark with distilled water. After standing for 10 minutes, the contents are filtered through Whatman No. 40 filter paper. Three milliliters of the mixed alkaline EDTA-formaldehyde solution are transferred to each of the colorimeter cuvetts. One-milliliter samples of the 0, 2, 4, 6, 8, and 10 milliequivalents per liter potassium working standards, and 1 ml. of the trichloroacetic acid filtrates of serum are transferred to their respective cuvetts. Three drops of gum ghatti are added to each tube, and the contents are mixed. One milliliter of tetraphenylboron solution is added rapidly to each cuvet by blowing vigorously with an Ostwald-Folin blow-out pipet. The contents are mixed by swirling and allowed to stand for 15 minutes. Absorbance readings are made at 420 m $\mu$  within 15 to 30 minutes after mixing.

**Calculation.**—A calibration chart is constructed by plotting the values for absorbance as ordinate, and the concentration of potassium as abscissa. The concen-

tration of potassium in the unknown serum is obtained by reference to the standard curve.

NOTE.—Normal values: 4.5 to 5.5 milliequivalents per liter.

## SULFONAMIDES

(Serum, Spinal Fluid, Urine)

**Reagents.** *n*-(1-Naphthyl)-ethylenediamine Dihydrochloride, 0.2% Solution.—Dye obtainable from Eastman Kodak Company, Rochester, N. Y. Keeps about 2 months in a brown bottle in the refrigerator. Do not use after it turns brown.

**Procedure.**—Place 0.5 ml. of serum in a test tube. Add 10 ml. of 10% trichloroacetic acid. Shake well and let stand 2 minutes. Centrifuge the test tube until the supernatant fluid is clear. To 1 ml. of the supernatant fluid add 2 ml. of distilled water. Add 1 ml. of 0.25% sodium nitrite solution. *Prepare fresh daily.* Mix well and let stand 3 minutes. Add 1 ml. of 1% ammonium sulfamate solution. Mix well and let stand 2 minutes. Add 1 ml. of 0.2% ethylenediamine dihydrochloride solution. Shake vigorously. Read in the spectrophotometer at 540 mμ. Obtain sulfonamide values in mg. per 100 ml. from calibration curve.

**Calculation.**—It is desirable to use calibration curves based on standards made from the drug being determined. If, in emergency, it is necessary to use a calibration curve made from a sulfa drug other than that used in the determination, the results must be multiplied by a factor based on the following formula:

$$\frac{\text{Molecular weight of drug being determined}}{\text{Molecular weight of drug used for curve}} = \text{factor}$$

To correct for the drug lost in precipitation of proteins with trichloroacetic acid, multiply the results obtained for sulfapyridine (if more than 5 mg. per 100 ml.), and for sulfathiazole by the factor 1.10.

**Calibration Curve.**—Sulfonamide stock standard solution (1 ml. = 0.5 mg.): Dissolve exactly 50 mg. of the pure sulfonamide powder (*not* tablets) in about 80 ml. of hot distilled water. Should the drug dissolve with difficulty, add 1 ml. of 1 N sodium hydroxide. Cool and dilute to volume with distilled water in a 100-ml. volumetric flask. This solution keeps indefinitely in the refrigerator.

From the stock standard solution make the following dilutions with distilled water in 50-ml. volumetric flasks:

<i>Stock Standard</i>	<i>Distilled Water to</i>	<i>Mg. per 100 ml. Sulfa. Represented</i>
1 ml.	50 ml.	1
2 ml.	50 ml.	2
6 ml.	50 ml.	6
10 ml.	50 ml.	10
20 ml.	50 ml.	20
28 ml.	50 ml.	28

To 0.5 ml. of each dilution, add 10 ml. of 10% trichloroacetic acid. Mix well. To 1 ml. of the mixture add 2 ml. of distilled water. Proceed as outlined above. Repeat several times on new dilutions made from new stock standards. Average the transmittance readings for each dilution and plot on semilogarithmic graph paper against mg. per 100 ml. of the sulfonamide used. The solubility of some of the sulfonamides is such that it may be necessary to use a 20 mg. per 100 ml. stock standard solution. In such event adjust accordingly the amounts used to make the dilute standards.

Sulfonamide	Optimum Blood Level, mg. 100 per ml.	Molecular Weight	Solubility *
Sulfanilimide.....	10-15	172	1480
Sulfapyridine.....	5-10	249	54
Sulfathiazole . . . .	4-10	255	96
Sulfadiazine . . . .	8-15	250	12.3
Sulfamerazine . . . .	10-15	265	170.0
Sulfaguanidine . . . .	3-5	232	220.0
Sulfasuxidine. . . . .	3	355	20.8
Sulfathalidine.....	1.5	403	Pract. insol.

\* Mg. per 100 ml. H<sub>2</sub>O at 37.5°C. and pH 7.1.

### TRANSAMINASES

#### SERUM GLUTAMIC OXALOACETIC TRANSAMINASE (SGO-T) AND SERUM GLUTAMIC PYRUVIC TRANSAMINASE (SGP-T) (Serum)

**Reagents.** *Aspartate-Glutarate Substrate (Alpha-ketoglutarate, 2 millimoles per liter, dl-aspartate 200 millimoles per liter).*—Place 29.2 mg. of alpha-ketoglutaric acid and 2.66 g. of dl-aspartic acid in a small beaker. Add 1 N NaOH until the solution is complete. Adjust to a pH of 7.4 with NaOH, transfer quantitatively with 0.1 M phosphate buffer (pH 7.4) to a 100-ml. volumetric flask and dilute to the mark with buffer.

*2,4-Dinitrophenylhydrazine (1 millimole per liter).*—Dissolve 19.8 mg. of 2,4-dinitrophenylhydrazine in 100 ml. of 1 N HCl.

**Standard Solution (Pyruvate, 2 millimoles per liter).**—Dissolve 22 mg. sodium pyruvate in 100 ml. of 0.1 M phosphate buffer (pH 7.4).

**Alanine-Alpha-ketoglutarate Substrate (Alpha-ketoglutarate, 2 millimoles per liter, dl-alanine 200 millimoles per liter).**—Place 29.2 mg. of alpha-ketoglutaric acid and 1.78 g. of dl-alanine in a small beaker. Add 1 N NaOH until solution is complete. Adjust to pH 7.4 with NaOH, transfer quantitatively with 0.1 M phosphate buffer to a 100-ml. volumetric flask, and then dilute to the mark with buffer solution.

**Procedure.** *SGO-T.*—Place 1 ml. of aspartate-glutarate substrate in a spectrophotometer cuvet (19 by 105 mm.) (one tube for each specimen) and place in 37° water bath and allow it to warm to desired temperature (37°C.). This takes 10 to 15 minutes. Add exactly 0.2 ml. of serum to the substrate. Shake gently to mix and replace in the water bath. Exactly 60 minutes after adding serum, add 1 ml. of 2,4-dinitrophenylhydrazine reagent. (This stops activity and starts the color reaction.) Shake gently and leave at room temperature. After 20 minutes, add 10 ml. 0.4 N sodium hydroxide (develops color). Mix by inversion using clean rubber stoppers. Let stand for 30 minutes and then read absorbance at 505 mμ in the spectrophotometer using distilled water as a reference.

Determine units of activity of SGO-T of the serum from the calibration curve. If the value is greater than 182 units per ml. of serum, repeat test after diluting serum with distilled water (1 ml. serum in 9 ml. of water). Value obtained with diluted serum is multiplied by 10 to get the correct value of SGO-T units per milliliter of serum.

**SGP-T.**—Place 1 ml. of alanine- $\alpha$ -ketoglutarate substrate in a spectrophotometer cuvet (19 by 105 mm.) and place in a 37° water bath and allow it to warm to desired temperature (37°C.). Add exactly 0.2 ml. of serum to the substrate. Shake gently to mix and replace in the water bath. Exactly 30 minutes after adding serum, add 1 ml. of 2,4-dinitrophenylhydrazine reagent. Shake gently and leave at room temperature. After 20 minutes, add 10 ml. of 0.4 N NaOH. Mix by inversion using clean rubber stoppers. Let stand for 30 minutes and then read absorbance at 505 m $\mu$  in the spectrophotometer using distilled water as a reference.

Determine the units of activity of the SGP-T of the serum from the calibration curve for SGP-T. Prepare the calibration for SGP-T as for SGO-T, substituting alanine- $\alpha$ -ketoglutarate substrate for aspartate glutarate substrate.

**Calibration Curve.**—Into spectrophotometer tubes, pipet the solution as indicated below.

Tube No.	Std. Soln., ml.	Prepared Substrate, ml.	Water, ml.	Units SGO Transaminase per Ml. Serum	Units SGP Transaminase per Ml. Serum
1	0	1.0	0.2	0	0
2	0.1	0.9	0.2	20	23
3	0.2	0.8	0.2	55	50
4	0.3	0.7	0.2	95	83
5	0.4	0.6	0.2	148	125
6	0.5	0.5	0.2	216	—

Add 1 ml. of 2,4-dinitrophenylhydrazine reagent to each tube. Shake gently and allow to stand for 20 minutes at room temperature. Add 10 ml. of 0.4 N NaOH to each tube. Mix by inversion using clean rubber stoppers. Thirty minutes after adding the NaOH, read and record the absorbances using water as reference at 505 m $\mu$ . Plot a calibration curve of absorbances vs. the corresponding units of transaminase. It will not necessarily be a straight line.

NOTES.—

	SGO-T Units per Ml. Serum	SGP-T Units per Ml. Serum
Normal values.....	8-40	5-35
Borderline.....	40-50	35-45
Elevated.....	Over 50	Over 45
Post infarction.....	40-200	40-100
Liver necrosis.....	2000	Over 100

Normal values (Molander *et al.*) are 5 to 40 units; Laennec's cirrhosis, 13 to 286 units; biliary cirrhosis, 57 to 330; and viral hepatitis, 540 to 1890 units.

## TRYPSIN (PROTEINASE)

(Duodenal Contents)

*Reagents.* 0.2 M Phosphate Buffer, pH 7.2.

5% Casein Solution.—Suspend 5 g. casein (Merck, according to Hammarsten) in about 50 ml. of water and then add 40 ml. of 0.1 N NaOH and sufficient water to make a total of 100 ml. This solution should be refrigerated and should be prepared fresh about every two weeks.

Digestion Mixture.—Prepared as for non-protein nitrogen determination.

Gum Ghatti.—Prepared as for non-protein nitrogen determination.

Nessler's Solution.—Prepared as for non-protein nitrogen determination.

Nitrogen Standard.—0.283 g. ammonium sulfate made up to 1000 ml. with water (0.3 mg. of nitrogen in 5 ml.).

*Procedure.*—Make a 1:50 dilution of duodenal contents as follows: 1 ml. duodenal contents is made up to 50 ml. by adding 10 cc. of buffer, pH 7.2, and distilled water.

Add 3 ml. of casein solution, 3 ml. of water, and 3 ml. of phosphate buffer to a test tube. Warm in water bath (38°C.) for 5 minutes. Add 1 ml. of 1:50 dilution duodenal contents. Mix thoroughly. Incubate in 38°C. water bath for 30 minutes. Add 2 ml. of 20% trichloroacetic acid. Filter. Place an aliquot (usually 3 ml.) of filtrate in an N.P.N. tube and proceed as for usual non-protein nitrogen determination.

Add 5 ml. of casein solution, 3 ml. of water, and 3 ml. of phosphate buffer solution (blank) to a test tube. Warm in water bath (38°C.) for 5 minutes. Incubate in 38°C. water bath for 30 minutes. Add 2 ml. of 20% trichloroacetic acid. Add 1 ml. of duodenal contents (1:50 dilution). Filter. Place 3 ml. of filtrate in an N.P.N. tube and proceed as for usual non-protein nitrogen determination.

To prepare the standard, place 5 ml. standard solution in an N.P.N. tube. Add 1 ml. of digestion mixture. Add 1 ml. of gum ghatti. Dilute to 35 ml. with water. Add 15 ml. of Nessler's reagent. Do not boil the standard.

Calculation.—

$$\frac{\text{Mg. per 100 ml. standard}}{\text{Mg. per 100 ml. unknown}} \times \frac{12}{\text{aliquot}} \times 0.3 = \text{mg. nitrogen produced in digestion}$$

$$\text{Test} - \text{blank} \times 21.3 = \text{trypsin expressed as \% of average normal}$$

NOTES.—Normal values: trypsin 45% to 148% of average normal. The sample to be analyzed is refrigerated from the time it is obtained from the patient to the time the analyses are to be made. Repeated studies have indicated that there is no significant alteration in enzyme activity of duodenal contents during a period of 24 hours, provided the sample is not strongly acid due to contamination with gastric juice. In such cases the results are quite unreliable even though the analyses are made immediately.

## UREA NITROGEN

(Serum and Urine)

*Reagents.* Stock Urea Nitrogen Standard.—Dissolve 64.2 mg. of urea, c.p., in distilled water. Dilute to 100 ml. with water in a volumetric flask. Mix well. One gram of urea nitrogen corresponds to 2.14 g. of urea; therefore, 30 mg. of urea nitrogen corresponds to 64.2 mg. of urea.

**Diacetylmonoxime Reagent.**—Dissolve 1 g. of diacetylmonoxime (Eastman No. 86) in 100 ml. of 5% acetic acid. Discard when a discoloration or precipitate appears. Store in a brown bottle at room temperature.

**Arsenic-Hydrochloric Acid Oxidizing Mixture.**—Dissolve 10 g. of crystalline arsenic acid ( $\text{H}_3\text{AsO}_4$ , B & A Reagent) in 100 ml. of concentrated HCl and allow to stand until clear.

**Procedure. Serum.**—Into a small Erlenmeyer flask place 8 ml. of 0.083 . . . *N* sulfuric acid and 1 ml. of serum, rinsing out the pipet by drawing in and expelling some of the mixture several times. Mix the contents of the flask by gentle rotation until the fluid is uniformly black-brown. Add 1 ml. of 10% sodium tungstate drop by drop while constantly but gently rotating the flask. Mix well. Add 10 ml. of distilled water and mix thoroughly. This is a 1:20 dilution. Filter and place 2 ml. of filtrate in a 20-ml. graduated test tube (Myers-Bailey Tube). In another 20-ml. graduated test tube place 2 ml. of distilled water. This is the blank. Add 2 ml. of diacetylmonoxime reagent and mix well. Add 3 ml. of arsenic-hydrochloric oxidant and mix well. Add 2 ml. of distilled water and mix well. Place in a boiling water bath for 20 minutes, covering the mouth of the tubes with marbles. Cool under running tap water for 3 minutes. Adjust the volume to 10 ml. with distilled water. Measure the transmittancy of the sample against the reagent blank set at 100% *T* at a wavelength of 475  $\text{m}\mu$  and obtain the concentration of urea nitrogen from the calibration curve. Use cuvetts, 12 by 75 mm.

**Urine.**—Filter a small portion of a thoroughly mixed urine specimen. Place 5 ml. of the filtered urine in a 100-ml. volumetric flask and dilute to volume with distilled water. Proceed as for blood, using 1 ml. of the 5:100 dilution instead of the blood. Multiply the value from the calibration curve for blood by 20 to obtain the concentration of urea nitrogen (mg.) in 100 ml. of urine.

$$\frac{\text{Urea nitrogen (mg./100 ml.)}}{1000} \times \frac{\text{volume (24-hour sample)}}{100} \times 2.14 = \text{urea (g./24 hours)}$$

For concentrations of urea nitrogen less than 200 mg. per 100 ml., use 10 ml. of urine above and multiply the values obtained from the calibration curve for blood by 10; for concentrations in excess of 1000 mg. per 100 ml., use 2.5 ml. of urine and multiply the values obtained by 40.

**Calibration Curve.**—Into a 100-ml. volumetric flask place 10 ml. of stock urea standard (0.3 mg. per ml.), and dilute to volume with distilled water. This dilute standard represents 0.03 mg. per ml. urea nitrogen. Prepare just before use.

In a series of five accurately calibrated 20-ml. graduated test tubes, place, respectively, 0, 0.5, 1, 1.5, and 2 ml. of dilute standard; and 2, 1.5, 1, 0.5 and 0 ml. of distilled water, respectively, bringing the volume in each tube to 2 ml. These standards represent concentrations of urea nitrogen equivalent to 0, 15, 30, 45, and 60 mg. per 100-ml. sample. Treat each calibration standard exactly as outlined above. Set the zero concentration standard at 100% *T* at a wavelength of 475  $\text{m}\mu$  and record the transmittancy of the 15, 30, 45, and 60 mg. per 100 ml. standard. Plot the observed values on semilogarithmic paper and prepare a calibration curve. The curve will be linear only to approximately 50 mg. per 100 ml. A new calibration curve is required each time new reagents are made up.

**NOTE.**—Normal values: 9 to 17 mg. per 100 ml. of serum.  
20 to 30 g. per 24-hour urine specimen.

## URIC ACID

### (Serum and Urine)

**Reagents.** **Uric Acid Reagent.**—Place 100 g. of molybdenum-free sodium tungstate, 70 ml. of phosphoric acid, and about 700 ml. of distilled water in a 1000 ml. Erlenmeyer flask. Boil gently for 2 hours under a reflux condenser. Cool and dilute to 1 liter.

**Stock Standard Uric Acid Solution** (1 ml. = 1 mg. uric acid).—Accurately weigh 1 g. of uric acid and transfer it to a liter volumetric flask by means of a dry funnel. Place about 0.6 mg. of lithium carbonate in a beaker containing 150 ml. of distilled water and shake until dissolved, about 5 minutes. Filter the carbonate solution and heat the filtrate to 60°C. With the hot carbonate solution rinse the uric acid into the flask and shake immediately. The flask may be heated additionally under hot running water. The lithium carbonate solution is not always clear even when filtered. This turbidity should not be mistaken for undissolved uric acid, which might result in unnecessary warming and shaking. In 5 minutes the uric acid should all be dissolved. Shake the flask under cool running water without undue delay. Add 20 ml. of c.p. formalin and half fill the flask with water and shake thoroughly. Add 3 ml. of glacial acetic acid. Shake and dilute to 1000 ml. Keep in tightly stoppered brown bottle in the dark. Keeps about one year.

**Dilute Standard Uric Acid Solution** (5 ml. = 0.025 mg. uric acid).—Dilute 1 ml. of stock standard uric acid solution to 200 ml. in a volumetric flask. Add 3 ml. of chloroform. Prepare fresh once a month. (Use to make calibration curve dilutions.)

**Procedure.** **Serum.**—Prepare a protein-free filtrate as follows: Place 14 ml. of water in a 50-ml. Erlenmeyer flask; add 2 ml. of 10% sodium tungstate; add 2 ml. of serum; mix; add slowly, with rotation, 2 ml. of 0.666 . . . *N* sulfuric acid; mix well; let stand 30 minutes, and filter. Place 10 ml. of filtrate in a 50-ml. Erlenmeyer flask. Add 5 ml. of distilled water. Add 5 ml. of 5% sodium cyanide solution. Add 0.5 ml. of uric acid reagent. Mix. Let stand 20 minutes. If cloudy, centrifuge for 5 minutes. Read in the spectrophotometer at a wavelength of 550  $m\mu$ . Set up a blank using 15 ml. of water, 5 ml. of 5% sodium cyanide, and 0.5 ml. of uric acid reagent.

**Urine.**—Measure total volume of urine. Make a 1:20 dilution of urine with distilled water. Place 10 ml. of the dilution in a 50-ml. Erlenmeyer flask and proceed as above.

**Calculations.**—Obtain values for uric acid in blood in mg. per 100 ml. from calibration curve. For urine, values taken from the calibration curve must be corrected for dilution and total volume of urine.

**Calibration Curve.**—In each of four 50-ml. Erlenmeyer flasks place the following:

Flask	Dilute Uric Acid Std., ml.	Distilled Water, ml.	Mg. per 100 ml. Uric Acid
1	2	13	1
2	4	11	2
3	8	7	4
4	12	3	6

To each flask add 5 ml. of 5% sodium cyanide solution. Mix. To each add 0.5 ml. of uric acid reagent. Mix. Allow to stand for 20 minutes. Read in the spectrophotometer at a wavelength of 550 using a blank made of 15 ml. of distilled water, 5 ml. of 5% sodium cyanide solution, and 0.5 ml. of uric acid reagent. Repeat several times with new dilutions so that an average of the readings will make a straight line when plotted on semilogarithmic graph paper. Plot average readings on semilogarithmic paper against uric acid values in mg. per 100 ml.

NOTES.—Normal values: 2 to 4 mg. per 100 ml. serum.  
0.4 to 1 g. per 24-hour urine.

Substances in the blood other than uric acid, such as ergothioneine and glutathione, give this blue color, but these are eliminated to a large extent by using serum for the test.

## UROBILINOGEN

(Urine and Feces)

**Reagents.** **Modified Ehrlich's Reagent.**—Place 0.7 g. of pure paradimethylaminobenzaldehyde in a 500-ml. Erlenmeyer flask. Add 75 ml. of concentrated hydrochloric acid and 75 ml. of distilled water.

**Stock Standard Dye Solution.**—Pontacyl Carmine 2B, 5 mg.; Pontacyl Violet 6 R (150%), 95 mg. Make up to 1 liter with 0.5% acetic acid. (Obtain the dyes from E. I. du Pont de Nemours Company, Wilmington, Delaware.)

**Procedure.** **Urine.**—Collect 24-hour specimen in a brown 1-gallon bottle containing about 100 ml. of petroleum ether and 5 g. of anhydrous sodium carbonate. Shake specimen to mix and measure the volume of urine after separation of the petroleum ether which has been added as a preservative. Place 50 ml. of urine in a 125-Erlenmeyer flask and add 25 ml. of freshly prepared 20% ferrous sulfate solution. Add 25 ml. of 10% sodium hydroxide with thorough mixing. Let stand 1 hour in the dark and then filter. (The remainder of the test must not be carried out in a brightly lighted room because light will destroy some of the urobilinogen.)

**Preliminary Test.**—Place 2 to 3 ml. of the filtrate in a test tube and acidify with an equal amount of modified Ehrlich's reagent. Add 4 to 6 ml. of a saturated solution of sodium acetate and notice the intensity of the developing color. If the color is very intense, use 1 ml. of the filtrate in the quantitative determination; if moderately intense, use 2 ml.; if pale-red, use 5 to 10 ml.; if faint, use 15 to 25 ml.; if absent, use 50 ml.

Dilute the amount of filtrate decided upon to 25 ml. (if less than that amount) and place in a small separatory funnel. Cover with approximately 50 ml. of pure petroleum ether which has been acidified with 5 ml. of glacial acetic acid. Immediately shake the mixture vigorously for several seconds. Allow the petroleum ether to separate; if an emulsion forms, it can be broken by the addition of more acetic acid or 1 to 2 ml. of 95% alcohol. Collect the aqueous fraction in another separatory funnel; then decant the petroleum ether into a clean separatory funnel. Extract the aqueous fraction twice more with 25-ml. portions of petroleum ether which is decanted as described above. Wash the combined petroleum ether extractions once with a small amount of distilled water. Discard the water. Extract the urobilinogen from the petroleum ether by vigorously shaking for 1 minute with 2 ml. of Ehrlich's reagent. Add 6 ml. of saturated aqueous solution of sodium acetate which brings out the maximum color in the



## 1130 CHEMICAL ANALYSIS IN CLINICAL MEDICINE

aqueous solution. Shake vigorously. Separate the colored solution into a 100-ml. graduated cylinder. Again shake the petroleum ether with the same amount of Ehrlich's reagent and sodium acetate solution and add the colored solution to the above. If more than a faint color develops, this procedure must be repeated until the extraction of urobilinogen is complete. Add water to the colored solution to make a volume convenient in calculation. Mix well. Prepare a blank consisting of 9 ml. of sodium acetate and 3 ml. of Ehrlich's reagent. Read in the spectrophotometer at a wavelength of 565  $m\mu$  using cuvetts (19 by 150 mm.) with the blank set at 100.

**Calculations.**—Obtain the value in mg. per 100 ml. from the calibration curve; then

$$\text{Mg. per 100 ml.} \times \frac{100}{50} \times \frac{\text{vol. of final sol.}}{\text{vol. of filtrate used}} = \text{mg. per 100 ml.}$$

Report in milligrams per 100 ml. and in milligrams per 24-hour specimen.

**Calibration Curve.**—Make a dilute standard dye solution by placing 20.4 ml. of the stock solution in a 100-ml. volumetric flask and diluting to volume with 0.5% acetic acid. (This dilute solution is equivalent to 0.6 mg. of urobilinogen in 100 ml.) Pipet the following amounts of dilute standard dye solution and 0.5% acetic acid in a series of cuvetts.

Dilute Dye Solution, ml.	0.5% Acetic Acid, ml.	Equivalent to Mg. of Dye per 100 ML.	Equivalent to Mg. per 100 ml. of Urobilinogen
0.84	19.16	0.085	0.025
1.67	18.33	0.17	0.05
3.34	16.66	0.34	0.10
5.00	15.00	0.51	0.15
6.67	13.33	0.68	0.20
8.34	11.66	0.85	0.25
10.00	10.00	1.02	0.30
13.34	6.66	1.36	0.40
16.66	3.34	1.70	0.50
20.00	0.00	2.04	0.60
0.00	20.00	Blank	0.00

Read each dilution in the spectrophotometer at a wavelength of 565  $m\mu$  with the blank set at 100. Repeat several times, average the results, and plot readings on semilogarithmic paper against their values in mg. per 100 ml. of urobilinogen.

**NOTE.**—Normal value: 0.2 to 3 mg. per 24-hour specimen.

**Feces.**—Weigh total specimen. Thoroughly mix the feces either in the carton, in a mortar, or in the electric mixer. Weigh out 10 g. of feces and place in a blender. Add 90 ml. of distilled water in small portions and mix. Allow the mixture to stand for a short time and decant the supernatant suspension into a liter Erlenmeyer flask containing 100 ml. of freshly prepared 20% ferrous sulfate

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For the standard carotene solution, read a solution containing 1  $\mu\text{g.}$  per ml. in heptane.

For the standard vitamin A solution, use 2 ml. of the heptane solution of the acetate containing 0.5  $\mu\text{g.}$  vitamin A per ml. Add 1 ml. water and 1 ml. N alcoholic KOH. Shake and treat as for the unknown.

Calculations.—

$$\frac{\text{Absorbance unknown (450 m}\mu\text{)}}{\text{Absorbance standard (450 m}\mu\text{)}} \times 200 = \mu\text{g. carotene/100 ml.}$$

$$\frac{\text{Drop in unknown absorbance at 325 m}\mu}{\text{Drop in standard absorbance at 325 m}\mu} \times 100 = \mu\text{g. vitamin A/100 ml.}$$

NOTES.—The extraction and centrifuging is carried out while ultraviolet light is excluded. This may be done by using red glassware or covering the containers with black paper. After irradiation the reading is practically zero, and this step may be omitted if the carotene level is not very high.

For irradiation, it is best to transfer the solution to 2-ml. capacity quartz test tubes tightly corked with corks rubbed with silicone grease, and wiped, to prevent evaporation. However, they may be effectively irradiated in the cuvettes covered with glass covers held in place by Scotch tape. A fan should be kept blowing on the containers to keep them cool during irradiation. A good arrangement is to suspend the tubes equidistant around a quartz lamp (about 5 cm. distant). From below, a small fan blows upward to cool the tubes. The blank is also irradiated. Mark the solvent level so that if evaporation should take place, the tubes can be made to volume again with heptane. It is best to irradiate the standard and determine the time required to obtain the lowest reading. This same time is used for the unknowns.

The normal vitamin A level is 15 to 60  $\mu\text{g.}$  per 100 ml. serum, and the normal carotene level is 120  $\mu\text{g.}$  per 100 ml. of serum.

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## Chapter 31

# COAL AND COKE

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### SAMPLING COALS CLASSED ACCORDING TO ASH CONTENT <sup>1</sup>

1. These methods cover procedures for the sampling of coal classified according to ash content, in order to obtain samples for analysis. Sampling procedures are prescribed for coals of the following ash groups:

Ash, %
Under 8
8.0 to 9.9
10.0 to 14.9
15.0 and over

For each ash classification there are eight size groups and for each size group these methods prescribe a minimum number of increments, each of a minimum weight which results in a specified minimum weight of gross sample.

Two procedures are recognized in this method, as follows:

- (1) *Commercial Sampling Procedure.*
- (2) *Special Purpose Sampling Procedure.*

NOTE 1.—For the determination of total moisture, two procedures are prescribed: one for a standard moisture sample which is obtained by splitting out a portion during the reduction of the gross sample; and the other a special moisture sample which requires a special procedure for handling the sample.

2. *Principles of Sampling and Precautions.*—It is imperative that every sample be collected and prepared carefully and conscientiously and in strict accordance with the procedures prescribed in these methods; for if the sampling is done improperly, the sample will be in error and it may be impossible or impracticable to take another sample. However, if the analysis is in error, another analysis can easily be made of the original sample.

Because of the many variations in the conditions under which coal must be sampled, and in the nature of the material being sampled, it is essential that the samples be collected by a trained and experienced sampler. Variations in the manner in which the coal is handled are such that it is impossible to specify rigid

<sup>1</sup> Under the standardization procedure of the Society, these methods are under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D192-48.

rules describing the exact manner of sample collection. Correct sampling principles must be applied to conditions as they are encountered.

The term "increment" as used in these methods designates that quantity of coal obtained by a single motion of the sampling instrument (Section 6). Due to variations in the structure, size consist, distribution of impurities, moisture, and the uneven distribution of sizes and impurities, care is required in the manner of collecting the increments. A complete cross-section of a stream or flow of coal (in motion) is generally the most representative.

The minimum weight of each increment is determined by the size of the coal as designated by round-hole screen.

The number of increments required for a given degree of accuracy depends upon the variability of the coal, and this variability increases with an increase of "free impurity." A coal with high inherent ash and comparatively little free impurity may show much less variability than a coal with a materially lower total ash, resulting from a low inherent ash and a high percentage of free impurity. For most practical purposes, an increase in total ash content usually indicates an increase in variability.

These methods prescribe a minimum number of increments and the minimum weight per increment required for eight size groups, each divided into four ash classifications.

It is essential that the increments be evenly distributed over the consignment.

TABLE 31-1. SIZE GROUPS

Group	Size Designation <sup>a</sup> (Round Hole Screens) Top Size Range	Grade of Coal <sup>b</sup>
1	$\frac{5}{8}$ in. and under	Resultants and sized coals
2	Over $\frac{5}{8}$ to $1\frac{1}{4}$ in., incl	Resultants and sized coals
3	Over $1\frac{1}{4}$ to 2 in., incl	Resultants and sized coals
4	Over 2 to 6 in., incl	Sized coals only
5	Over 2 to 4 in., incl	Resultants only
6	Over 4 to 6 in., incl	Resultants only
7	Top size designation over 6 in., and bottom size designation $\frac{5}{8}$ in. or over	Lump, block, or sized coals
8	Top size designation over 6 in.	Run-of-mine and resultants
	Top size designation over 6 in., and bottom size designation under $\frac{5}{8}$ in.	Lump, block, or sized coals

<sup>a</sup> The "top size" dimension indicates all coals with such size consist as classify them under the group in accordance with the provisions of Section on Size Designation of the Method for Designating the Size of Coal from Its Screen Analysis (ASTM D431, p. 1233).

<sup>b</sup> The term "resultant" indicates a commercial grade of coal whose size consist is essentially produced as a through-product of but one screen. The term "sized coal" indicates a commercial grade of coal whose size consist is essentially produced as a material passing through one screen and retained upon another.



(c) For lots over 1000 tons, any of the following alternatives may be used:

(1) Separate gross samples may be taken for each 1000 tons of coal or fraction thereof, and a calculated average (weighted) of the analytical determinations obtained on these prepared samples may be used to represent the lot (Note 2).

(2) Separate gross samples may be taken for each 1000 tons or fraction thereof, and the -20-mesh or -60-mesh samples obtained from such gross samples may be mixed together in proportion to the tonnage represented by each sample and one analysis carried out on the composite sample (Note 2).

(3) One gross sample may be used to represent the lot, provided that at least four times the minimum number of increments prescribed in Table 31-2 are taken.

NOTE 2.—Analyzing each sample separately and averaging the results of all samples each obtained from a 1000 ton lot or fraction thereof will give greater accuracy than obtained by making one analysis on a composite sample made up by mixing together, in the correct proportions, the -20-mesh or -60-mesh samples representing the 1000 ton lot or fraction thereof.

**5. Special Purpose Sampling Procedure.**—The special purpose sampling procedure shall apply to the sampling of coal when special accuracy is required, such as, classification by grade or rank (p. 1254), or performance tests.

To obtain a greater accuracy in the collection of the gross sample, increase the increment requirements prescribed in Table 31-2 according to the following rules:

<i>To Increase Accuracy of Collection of the Gross Sample (In 95 out of 100)</i>	<i>Increase Minimum Number of Increments Given in Table 31-2</i>
±5% of the ash content of the coal sampled. . . . .	4 times
±3.33% of the ash content of the coal sampled. . . . .	9 times

**6. Increments.**—(a) The term “increment” as used in these methods designates that quantity of coal obtained for the sample by a single motion of the sampling instrument, such as swinging it through a stream of coal or digging into the top of a carload. It is recommended that where possible the coal be sampled while in motion. Whenever it is necessary to carry out “top sampling” of railroad cars or piles, it shall be stated in the report that “top sampling” was employed. By top sampling is meant the collection of the gross sample from a series of holes or trenches dug below the surface of the coal before any portion of the contents of the car has been removed.

(b) The increments shall be regularly and systematically collected so that the entire lot of coal sampled will be represented proportionately in the gross sample. Each increment shall be collected by passing the sampling instrument through a stream of coal or digging into a pile with the same motion and requiring approximately the same time interval to complete the motion. The increments shall be collected at such frequency that not less than the specified minimum number of increments are taken. The best possible increment is one which cuts entirely a falling stream of the coal by means of a suitable receptacle passed at a uniform speed, the same for each increment, into one side of the stream and out the other, without allowing the receptacle to overflow.

(c) The gross sample should contain the same proportion of lump coal, small coal, and impurities as is contained in the lot of coal being sampled.

(d) The method of collecting the increments shall fulfill the requirements of paragraphs (a), (b) and (c). In every individual case, the method of collecting the increment shall be suited to the existing conditions and experience with the variation of these conditions shall be used to govern the procedure.

(e) It is well established that variations in flow, structure, or size consist of the coal, or in distribution of impurities, may make it impracticable to collect increments of minimum weights specified herein. In such cases, it will be necessary to collect an increment of greater weight in order to conform to the requirements prescribed in paragraphs (b) and (c).

(f) Sampling equipment is often not suitable or available for handling large lumps (8-in. cube and over) without obtaining a disproportionate amount of lump or small coal in the sample. Therefore, it is sometimes impossible because of practical considerations to collect an increment in strict agreement with the procedure specified in paragraphs (b), (c), and (d). For instance, in some cases it would require the stopping of a conveyor or a crane. In most cases it would result in increments many times the minimum weight specified. Whenever possible, the method of collecting the increment shall be in a manner not to exclude any fraction of the increment as collected. In no case shall the method of collecting the increment be such as to exclude lumps up to 25 pounds in weight (8-in. cube). When the coal is extremely lumpy it is best to break down the extremely large lumps before the increment is taken. If this is impossible or impractical, an increment as collected may contain lumps of such large size that in the experience of the sampler this increment would contribute an excessive proportion of lump to the gross sample. In such cases the proportion of lump that should be included in the gross sample shall be estimated; the large lumps shall be broken to pass an approximately 4-in. round-hole screen; and an aliquot portion selected for inclusion in the gross sample. The remainder of the lumps shall be discarded.

NOTE 3.—Whenever the size consist is known or can be determined, individual samples of lump and small coal may be collected and the sample for analysis shall be prepared by mixing together in correct proportions the -20-mesh or -60-mesh samples representing the individual samples of lump and small coal.

(g) Provision should be made for the preservation of the integrity of the sample.

**7. Reduction of Gross Samples.**—(a) Reduce the gross samples for analysis by mechanical preparation as described in the following paragraphs (b) to (e).

(b) Crush before dividing the gross samples of coal containing pieces  $\frac{3}{8}$  in. and larger so that at least 95% by weight will pass through a 4760-micron (No. 4) sieve and 100% will pass through a  $\frac{3}{8}$ -in. round-hole screen. Gross samples of coal of which 100% passes through a  $\frac{3}{8}$ -in. round-hole screen and less than 95% by weight passes through a 4760-micron (No. 4) sieve, may be divided before crushing to not less than 60 pounds by passing it through a riffle sampler or its equivalent as described in paragraph (c).

Gross samples of coal of which 100% passes through a  $\frac{3}{8}$ -in. round-hole screen and 95% or more by weight passes through a 4760-micron (No. 4) sieve, may be reduced in quantity to not less than 30 pounds by passing it through a riffle sampler or its equivalent as described in paragraph (c).

Should the performance of the primary crusher yield a product of which 100% will pass through a 4760-micron (No. 4) sieve or 95% through a 2380-micron (No. 8)

sieve, then some of the intermediate crushing operations will be unnecessary. However, follow the requirements of paragraphs (c), (d), and (e), in respect to the relation of the weight of the sample to the openings of the riffle sampler.

(c) Reduce the entire gross sample in quantity, crushed as described under paragraph (b), to not less than 30 pounds by passing it through a riffle sampler or its equivalent. The riffle sampler shall have openings of not less than  $\frac{3}{4}$  in. and not more than 1 in. Two types of riffle samplers suitable for reducing the sample as specified are shown in Fig. 31-1.

(d) Crush the sample of not less than 30 pounds (paragraph (c)) so that 100% will pass through a 4760-micron (No. 4) sieve, and then divide it by passing it through a riffle sampler with openings not less than  $\frac{1}{2}$  in. and not more than  $\frac{3}{4}$  in., obtaining a sample of not less than 15 pounds. Two types of riffle samplers suitable for reducing the sample as specified are shown in Fig. 31-2.

(e) Further crush the sample of not less than 15 pounds (paragraph (d)) so that 95% or more by weight will pass through a 2380-micron (No. 8) sieve. If the sample of not less than 15 pounds appears wet, air dry it before crushing it so that 95% will pass through a 2380-micron (No. 8) sieve, as it is not practicable to crush wet coal to pass this size sieve. Then divide the sample by passing it through a riffle sampler with openings not over  $\frac{1}{2}$  in. no more than three times, obtaining a sample of not less than  $1\frac{3}{4}$  pounds. Two types of riffle samplers suitable for reducing the sample as specified are shown in Fig. 31-2. However, if the determination of total moisture is of any significance, place the entire sample of not less than 15 pounds of wet coal in an airtight container for transmittal to the laboratory.

**8. Sampling for Determination of Total Moisture.**—When it is desired to report the "total moisture" of coal, either a "standard moisture sample" or a "special moisture sample" shall be used.

(a) **Standard Moisture Sample.** The standard moisture sample shall be used for the average commercial determination of total moisture, such as for control of preparation processes and for purchase specifications. The standard moisture sample, obtained from the gross sample in accordance with Section 9, shall be obtained from coals that are not too wet for crushing to -4 mesh.

(b) **Special Moisture Sample.** The "special moisture sample" shall be used for the determination of total moisture when special accuracy is required such as for classification by rank and grade or performance tests. It shall also be used for coals that are too wet to crush to -4 mesh, and is especially suitable for coals containing a high percentage of inherent moisture.

**9. Procedure for Standard Moisture Sample.**—(a) Obtain the standard moisture sample from the gross sample collected in accordance with Sections 2 to 7, inclusive, taking the precautions prescribed in the following paragraphs (b) to (e) in order to minimize moisture losses during collection and reduction of the gross sample.

(b) In collecting, handling, and reducing the sample, perform all operations rapidly as it has been found that moisture loss depends on several factors other than total moisture content, such as time required for crushing, atmospheric temperature and humidity, banded ingredients, and type of crushing equipment.

(c) While awaiting preparation, protect the uncrushed sample from moisture change due to exposure to rain, snow, wind, and sun by covering the sample with a tarpaulin. Do not hold the uncrushed sample longer than 3 hours before crushing unless the weight of the original sample as taken is recorded and the moisture loss or gain determined before the sample is crushed.

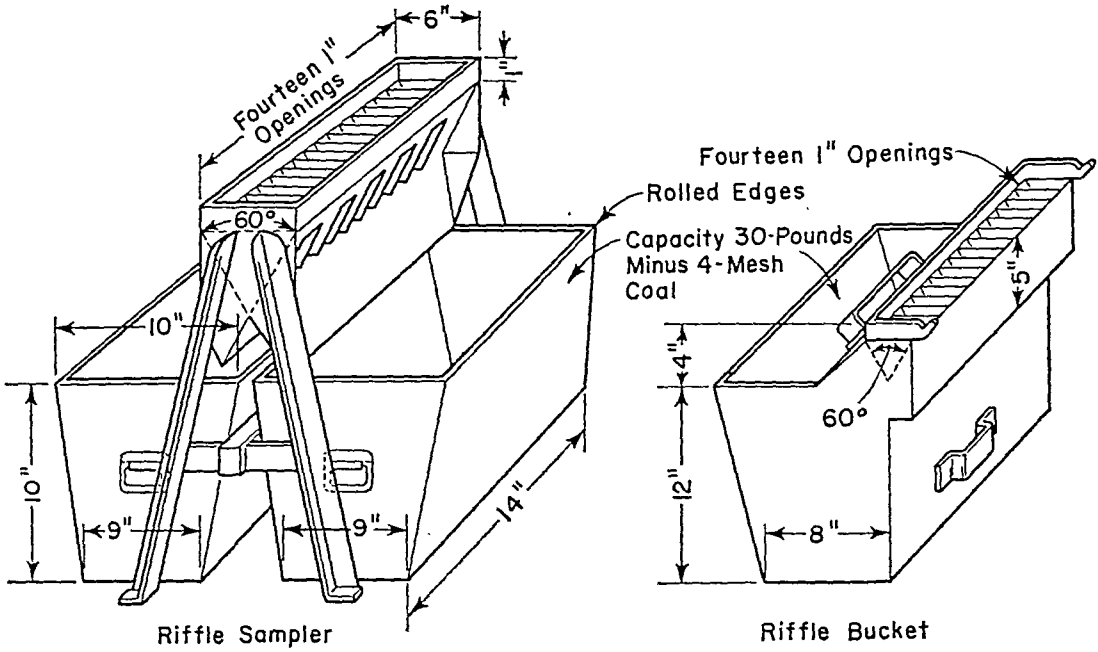


FIG. 31-1. Types of Riffle Samplers Suitable for Reduction Procedure Specified in Section 7(c).

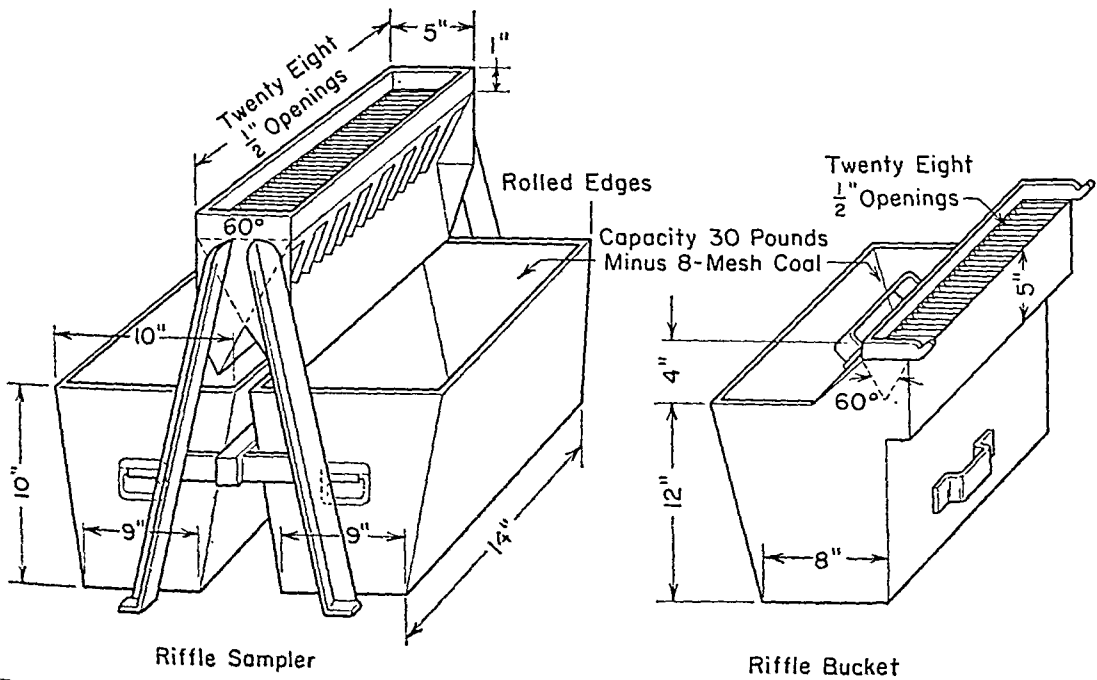


FIG. 31-2. Types of Riffle Samplers Suitable for Reduction Procedure Specified in Section 7(d) and (e).

(d) Follow the reduction procedure prescribed in Section 8 except that the crushing and riffing operations shall be carried out as rapidly as possible. Store temporarily any crushed or riffled portions that have to be held in waterproof containers with covers (such as standard 10-gallon milk cans) until the time of final preparation.

(e) Place the sample of not less than  $1\frac{3}{4}$  pounds of -8 mesh obtained during the reduction of the gross sample (Section 7(e)) in an airtight container for transmittal to the laboratory. However, if the coal is too damp for crushing to pass a 2380-micron (No. 8) sieve, place the entire sample of not less than 15 pounds of -4 mesh (Section 7(d)) in an airtight container for transmittal to the laboratory.

**10. Procedure for Special Moisture Sample.**—(a) The "special moisture sample" differs from the "standard moisture sample" in the method of collecting the sample, but the same precautions for collecting, handling, and reducing the sample outlined in Section 9(b) to (e) shall be followed.

(b) *Using Standard Gross Sample.* When special accuracy is required on samples that are not too wet to crush to -4 mesh, the "special moisture sample" shall be collected from the gross sample as follows: Remove small increments of the crushed coal from the reject discharge of the crusher or riffle sampler (or its equivalent) and place them immediately in a waterproof container with tight-fitting cover. Each increment shall be about  $\frac{1}{2}$  pound in weight. Take a sufficient number of  $\frac{1}{2}$ -pound increments for a minimum of 30 pounds to be collected for the special moisture sample. Evenly space the increments over the entire crushing or riffing period so as to be representative of the entire gross sample. Fill the container substantially, and make it airtight for transmitting the sample to the laboratory.

(c) *Using Separately Collected Sample.* For coals that are too wet to handle without a substantial moisture loss or cannot be crushed to -4 mesh, the special moisture sample shall be collected as follows, this procedure being particularly applicable for coals of 2-in. top size and smaller. Collect separate increments, in addition to those obtained for the gross sample. Place these increments in waterproof containers with tight-fitting covers (such as 10-gallon milk cans). Collect a minimum of 15 increments regularly and systematically so that the entire lot of coal being sampled will be represented proportionately in the special moisture sample. The minimum weight of each increment shall conform to the requirements prescribed in Table 31-2. Fill the container substantially, and make it airtight for transmitting the sample to the laboratory.

**11. Handling of Moisture Samples in Laboratory.**—The entire moisture sample as received in the laboratory, which shall have been collected as set forth in Sections 9 and 10, shall be air-dried in accordance with the conditions prescribed in Section 4 of the Methods of Laboratory Sampling and Analysis of Coal and Coke (ASTM D271, p. 1148). After air-drying, if the moisture sample is greater in weight than  $1\frac{3}{4}$  pounds, the sample shall be reduced in accordance with Section 7 to  $1\frac{3}{4}$  pounds, and the resulting  $1\frac{3}{4}$  pounds shall be crushed to 20 mesh. The moisture at 105°C. shall then be determined in accordance with Section 3 of Methods D271.

**12. Calculation.**—The total moisture shall be calculated in accordance with the section on the determination of moisture, page 1150.

## LABORATORY SAMPLING AND ANALYSIS OF COAL AND COKE <sup>3</sup>

1. These methods cover procedures for laboratory sampling and analysis of coal and coke. The procedures appear in the following order:

	<i>Sections</i>
Preparation of laboratory samples.....	2 to 7
METHODS OF ANALYSIS	
Purity of reagents.....	8
Moisture.....	9 to 12
Ash.....	13 to 15
Volatile matter.....	16 to 19
Fixed carbon.....	20
Sulfur:	
Eschka Method.....	21 to 24
Bomb Washing Method.....	25 and 26
Sodium Peroxide Fusion Method.....	27 to 29
Phosphorus in ash.....	30 to 32
Ultimate analysis:	
Carbon and hydrogen.....	33 to 38
Nitrogen.....	39 to 44
Oxygen.....	45
Calculation of analyses to dry basis.....	46
Reproducibility of results.....	47
Deterioration of coal samples.....	48

### PREPARATION OF LABORATORY SAMPLES

**2. Apparatus for Sampling Coal. Air-Drying Oven.**—An oven for air-drying wet samples. A suggested form is shown in Fig. 31-3. Such an oven is not essential, but is economical where many samples are to be dried.<sup>4</sup>

**Pans for Air-Drying Wet Samples.**—Galvanized iron pans 18 by 18 in. by 1.5 in. in depth.

**Balance or Scale.**—A balance or scale having a capacity of 5 kg. and sensitive to 0.5 g. for weighing the galvanized iron pans with samples.

**Crusher.**—A jaw crusher suitable for crushing coarse samples to pass a No. 4 (4760 micron) sieve.

**Grinder.**—A roll crusher or coffee-mill type of grinder suitable for reducing the material passing a No. 4 sieve to pass a No. 20 (840 micron) sieve. To reduce the moisture loss while crushing, a coffee-mill type of grinder should be entirely enclosed and have an enclosed hopper and receptacle capable of holding 15 pounds of coal.

<sup>3</sup> Under the standardization procedure of the Society, these methods are under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D271-58.

<sup>4</sup> For details of the air-drying oven, see A. C. Fieldner and W. A. Selvig, "Methods of Analyzing Coal and Coke," U. S. Bureau of Mines, *Bulletin No. 492*, p. 2 (1951).

**3. Apparatus for Sampling Coke.** Pans for Total Moisture Determination.—Galvanized iron pans 24 by 24 by 4 in. in depth.

**Balance or Solution Scale.**—A balance or scale having a capacity of 10 kg. and sensitive to 1 g. for weighing the galvanized iron pans with samples.

**Crusher.**—See Section 2.

**Roller-Crusher.**—A hard-steel roll crusher suitable for reducing the material passing a No. 4 sieve to pass a No. 20 sieve.

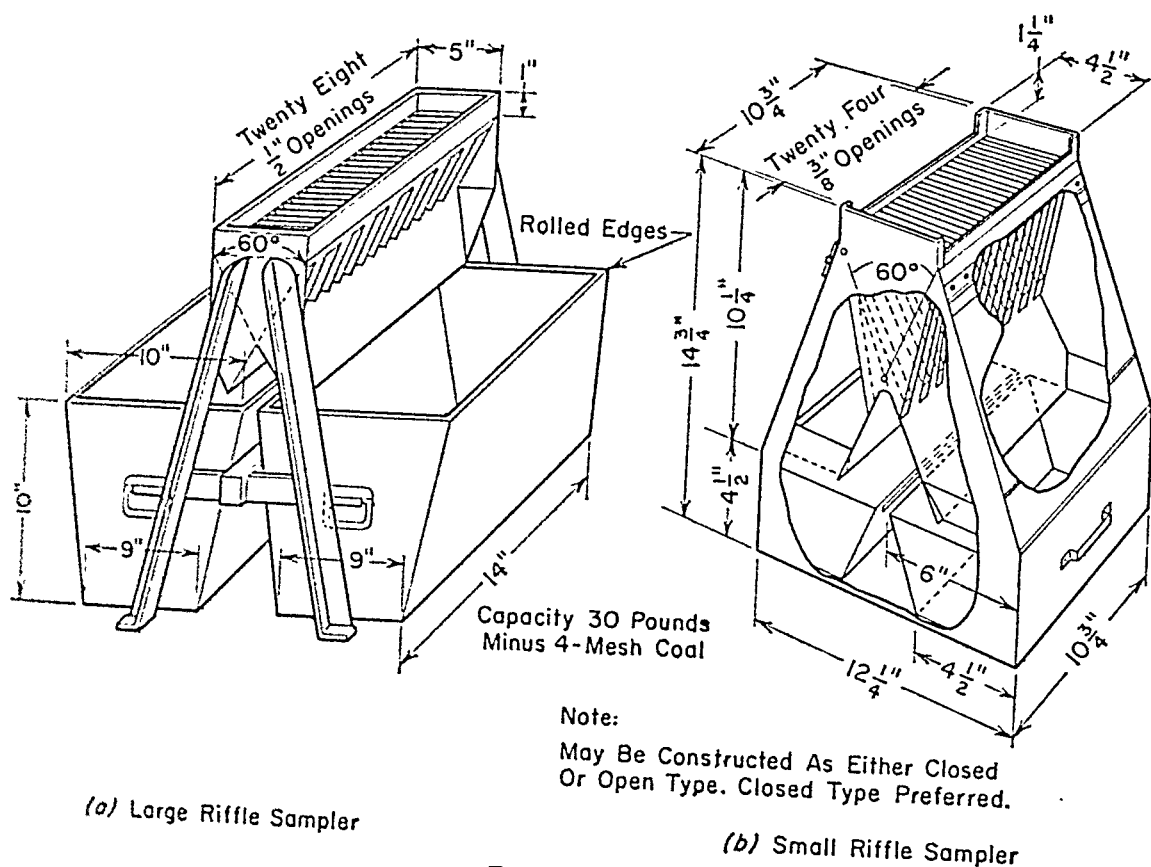


FIG. 31-4.

**Pulverizer.**—A porcelain jar ball mill, hard-steel roll crusher, or hard-steel diamond mortar for reducing the product passing a No. 20 sieve to pass a No. 60 sieve. The porcelain jars for the ball mill should be approximately 9 in. in diameter and 10 in. in height. The flint pebbles should be smooth, hard, and well-rounded. The rolls of the hard-steel roll crusher should revolve at the same speed.

**Large Riffle Sampler.**—See Section 2.

**Small Riffle Sampler.**—See Section 2.

**Sieves.**—See Section 2.

**Containers.**—See Section 2.

**Oven, Stove, or Hot Plate.**—An oven, stove, or hot plate for drying coke samples in the determination of total moisture. If an oven is used, it should have openings provided for natural ventilation and should be capable of being regulated between 104° and 200°C. If the coke is dried on a stove or hot plate, a thermometer should be placed in it, and care exercised that the temperature does not exceed 200°C. at any point in the pan of coke.

**Pulverizer.**—A porcelain jar ball mill, planetary disc crusher, chrome-steel bucking board, or any satisfactory form of pulverizer for reducing the material passing a No. 20 sieve to pass a No. 60 (250 micron) sieve. The porcelain jars for the ball mill should be approximately 9 in. in diameter and 10 in. in height. The flint pebbles should be smooth, hard, and well rounded.

**Large Riffle Sampler.**—A large riffle sampler with  $\frac{1}{2}$ - or  $\frac{3}{4}$ -in. divisions for reducing the coal passing the No. 4 sieve to 15 pounds (see Fig. 31-4 (a)).

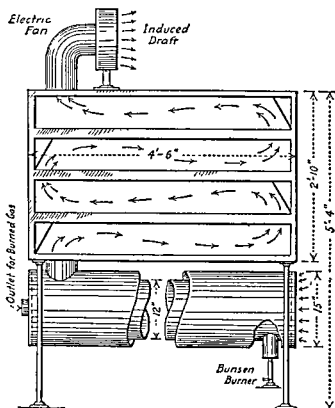


FIG. 31-3. Drier for Coarse Samples. The outlet for air at the top may be connected with a chimney or any other device which will furnish a suitable draft. (*Bulletin No. 9, Geological Survey of Ohio, p. 312.*)

**Small Riffle Sampler.**—A small riffle sampler with  $\frac{1}{4}$ - or  $\frac{3}{8}$ -in. divisions for reducing the material passing the No. 20 and the No. 60 sieves to a laboratory sample (see Fig. 31-4 (b)).

**Sieves.**—In addition to the sieves mentioned above, include a No. 60 sieve with cover and receiver. The sieve designations employed in these methods are those of the Specifications for Sieves for Testing Purposes (ASTM E11, p. 1277), and all sieves shall conform to the detailed requirements of these specifications.

**Containers.**—Samples in which the moisture content is important should always be shipped in moisture-tight containers. A galvanized iron or tin can with an airtight friction top or a screw top that is sealed with a rubber gasket and adhesive tape is best adapted to this purpose. Glass fruit jars sealed with rubber gaskets may be used, but require very careful packing to avoid breakage in transit. Samples in which the moisture content is of no importance need no special protection from loss of moisture.



**3. Apparatus for Sampling Coke.** Pans for Total Moisture Determination.—Galvanized iron pans 24 by 24 by 4 in. in depth.

**Balance or Solution Scale.**—A balance or scale having a capacity of 10 kg. and sensitive to 1 g. for weighing the galvanized iron pans with samples.

**Crusher.**—See Section 2.

**Roller-Crusher.**—A hard-steel roll crusher suitable for reducing the material passing a No. 4 sieve to pass a No. 20 sieve.

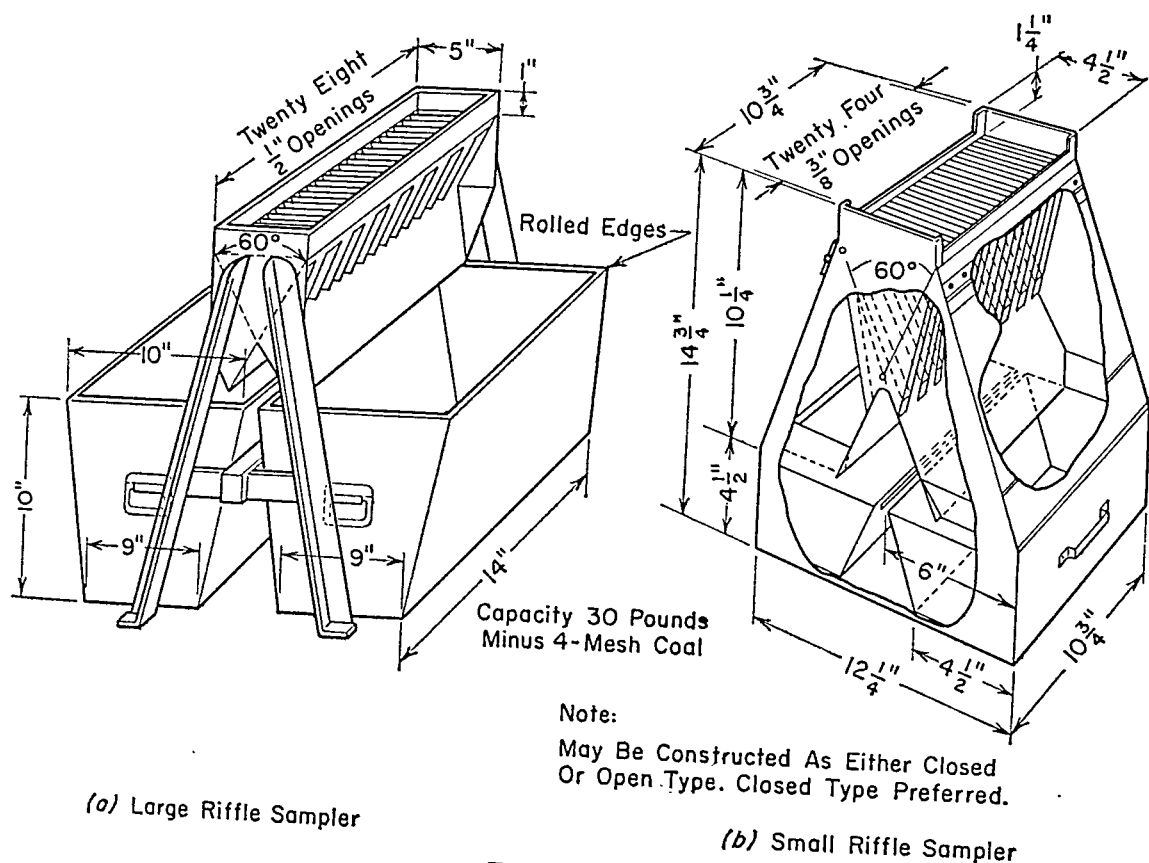


FIG. 31-4.

**Pulverizer.**—A porcelain jar ball mill, hard-steel roll crusher, or hard-steel diamond mortar for reducing the product passing a No. 20 sieve to pass a No. 60 sieve. The porcelain jars for the ball mill should be approximately 9 in. in diameter and 10 in. in height. The flint pebbles should be smooth, hard, and well-rounded. The rolls of the hard-steel roll crusher should revolve at the same speed.

**Large Riffle Sampler.**—See Section 2.

**Small Riffle Sampler.**—See Section 2.

**Sieves.**—See Section 2.

**Containers.**—See Section 2.

**Oven, Stove, or Hot Plate.**—An oven, stove, or hot plate for drying coke samples in the determination of total moisture. If an oven is used, it should have openings provided for natural ventilation and should be capable of being regulated between 104° and 200°C. If the coke is dried on a stove or hot plate, a thermometer should be placed in it, and care exercised that the temperature does not exceed 200°C. at any point in the pan of coke.

**4. Sample Preparation for Coal Appearing Dry.**—Crush the sample that has been collected and reduced in accordance with the Methods of Sampling Coals Classed According to Ash Content (p. 1137) by passing through rolls or an enclosed grinder adjusted so that the product will pass a No. 20 sieve. Take a 50-g. total moisture sample, without sieving, immediately after the material has passed through the crushing apparatus. This sample should be taken with a spoon from various parts of the product passing a No. 20 sieve, and should be placed directly in a rubber-stoppered bottle.

Thoroughly mix the main portion of the sample, reduce on the small riffle sampler to about 200 g., and pulverize to pass a No. 60 sieve by any suitable apparatus without regard to loss of moisture. After all the material has been passed through the No. 60 sieve, mix, and divide it on the small riffle sampler to about 50 g. Transfer the final sample to a 4-ounce rubber-stoppered bottle. Determine moisture in both the No. 60 sieve sample and the No. 20 sieve sample in accordance with Sections 9, 10, 11 and 12.

NOTE 1.—Samples crushed to pass a No. 4 sieve, prepared in accordance with the Methods of Sampling Coals Classed According to Ash Content, may be crushed to pass a No. 8 (2380 micron) sieve and reduced to not less than  $1\frac{3}{4}$  pounds in accordance with Section 7(e) of Methods D492, p. 1142.

**5. Sample Preparation for Coal Appearing Wet.**—Spread the sample on tared pans, weigh, and air-dry at room temperature, or in the special drying oven shown in Fig. 31-3 at 10° to 15°C. above room temperature, and weigh again (Note 2). Continue the drying until the loss in weight is not more than 0.1% per hour. Drying should not be continued beyond this point because of the oxidation of the coal. Complete the sampling as described in Section 4 for dry coal.

NOTE 2.—Freshly mined or wet coal loses moisture rapidly on exposure to the air of the laboratory; hence the sampling operations between opening the container and taking the total-moisture sample passing a No. 20 sieve must be conducted with the utmost dispatch and with minimum exposure to air.

**6. Sample Preparation of Coal Appearing Wet or Dry, Ball-Mill Method.**—This method of sampling<sup>5</sup> does not require a total moisture sample of the coal passing a No. 20 sieve as do the methods described in Sections 4 and 5. The coal is first air-dried to bring it to a condition of approximate equilibrium with the air to minimize moisture change during the preparation of the sample for analysis. After air-drying, all operations are performed with the utmost dispatch to prevent moisture change. Fine grinding of the sample is done in an airtight ball mill. Total moisture is calculated from the air-drying loss and the residual moisture in the sample prepared for analysis.

Spread the sample on tared pans, weigh, and air-dry in the special moisture oven shown in Fig. 31-3 at 10° to 15°C. above room temperature until the loss in weight between two successive weighings made 6 to 12 hours apart does not exceed 0.1% per hour. Drying should not be continued beyond this point because of the oxidation of the coal. Record the loss in weight as "air-drying loss."

Immediately after the final weighing, quickly crush the entire sample<sup>5</sup> by means of a roll crusher adjusted so the product will pass a No. 20 sieve. Then, without sieving, quickly reduce the coal on the small riffle sampler to about 200 g. Put

<sup>5</sup> This method of sampling is used by the U. S. Bureau of Mines, see A. C. Fieldner and W. A. Selvig, "Methods of Analyzing Coal and Coke," U. S. Bureau of Mines, *Bulletin No. 492*, p. 1 (1951).

by impact in a hard-steel diamond mortar. The use of rubbing surfaces such as a disc pulverizer or a bucking board is never permissible for grinding coke.

NOTE 3.—The accuracy of the method of preparing laboratory samples should be checked frequently by resampling the rejected portions and preparing a duplicate sample. The ash in the two samples should not differ by more than 0.4%.

### METHODS OF ANALYSIS

NOTE 4.—Results of analyses may be calculated to the dry coal basis as provided in Section 46.

8. *Purity of Reagents.*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>7</sup> Other grades may be used provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to the Specifications for Reagent Water (ASTM Designation: D1193).

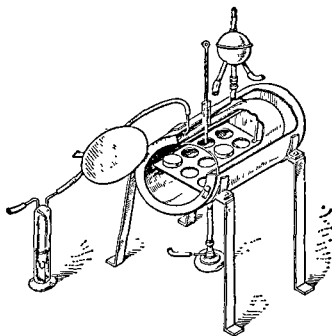


FIG. 31-5. Toluene or Glycerol and Water Oven for Determining Moisture (*Bulletin No. 492*, U. S. Bureau of Mines, p. 6, 1951).

### MOISTURE

9. *Apparatus.* Moisture Oven, for Coal.—For determining the moisture of coal, the oven shall be so constructed as to have a uniform temperature in all parts and a minimum of air space. It may be of the form shown in Fig. 31-5. Provision shall be made for renewing the air in the oven at the rate of two to four times a minute, with the air dried by passing it through sulfuric acid.

<sup>7</sup> "Reagent Chemicals, American Chemical Society Specifications," Am. Chem. Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., Princeton, N. J., and the "United States Pharmacopoeia."

**Moisture Oven, for Coke.**—For determining the moisture of coke, an ordinary drying oven with openings for natural air circulation and capable of temperature regulation between limits of 104° and 110°C. may be used.

**Capsules with Covers.**—A convenient form, which allows the ash determination to be made on the same sample, is a porcelain capsule,  $\frac{7}{8}$  in. in depth and  $1\frac{3}{4}$  in. in diameter, or a fused silica capsule of similar shape. This shall be used with a well-fitting flat aluminum cover, illustrated in Fig. 31-6. Platinum crucibles or glass capsules with ground-glass caps may also be used. They should be as shallow as possible, consistent with convenient handling.

**10. Materials. Desiccant.**—Sulfuric acid ( $\text{H}_2\text{SO}_4$ , sp. gr. 1.84).

**11. Procedure for Coal or Coke Passing a No. 60 Sieve.**—Heat the empty capsules under the conditions at which the sample is to be dried, place the stopper or cover on the capsule, cool over sulfuric acid for 30 minutes, and weigh. Dip out with a spoon or spatula from the sample bottle approximately 1 g. of the sample. Put this quickly into the capsule, close, and weigh at once.

An alternate procedure for weighing out the sample (more subject to error) is as follows: After transferring an amount of the sample slightly in excess of 1 g., bring to exactly 1 g. in weight ( $\pm 0.5$  mg.) by quickly removing the excess weight of the sample with a spatula. The utmost dispatch must be used in order to minimize the exposure of the sample until the weight is found.

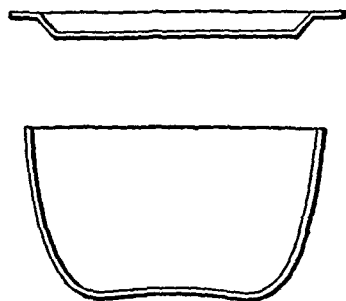


FIG. 31-6. Capsule for Use in Determining Moisture.

After removing the covers, quickly place the capsules in a preheated oven (at 104° to 110°C.) through which passes a current of air dried by sulfuric acid (sp. gr. 1.84) (the current of dry air is not necessary for coke). Close the oven at once and heat for 1 hour. Open the oven, cover the capsules quickly, cool in a desiccator over sulfuric acid (sp. gr. 1.84), and weigh.

Use the percentage of moisture in the sample passing a No. 60 sieve to calculate the results of the other analyses to a dry basis.

**12. Procedure for Coal Passing a No. 20 Sieve.**—Use 5 g. of the sample, weighed to the nearest 2 mg., and heat for  $1\frac{1}{2}$  hours. Complete the determination as described in Section 11.

### ASH

**13. Apparatus. Gas or Electric Muffle Furnace for Coal.**—For determination of ash of coal, the muffle shall have good air circulation and be capable of having its temperature regulated between 700° and 750°C.

**Gas or Electric Muffle Furnace or Meker Burner for Coke.**—For determination of ash of coke, the muffle shall have good air circulation and be capable of having its temperature regulated not to exceed 950°C.

**Porcelain Capsules.**—Porcelain capsules,  $\frac{7}{8}$  in. in depth, and  $1\frac{3}{4}$  in. in diameter, or similar shallow dishes or platinum crucibles.

**14. Procedure for Coal.**—Place the porcelain capsules containing the dried coal from the moisture determination in a cold muffle furnace, or on the hearth at a low temperature, and gradually heat to redness at such a rate as to avoid mechanical loss from too rapid expulsion of volatile matter (Note 5). Finish the ignition to constant weight ( $\pm 0.001$  g.) at a temperature between 700° and 750°C. Cool in a desiccator, and weigh as soon as cold. (Notes 6 and 7).

NOTE 5.—Before replacing the capsules in the muffle for ignition to constant weight, the ash should be stirred with a platinum or Nichrome wire. Stirring once or twice before the first weighing hastens complete ignition.

NOTE 6.—The result obtained by this method is "uncorrected" ash. For "corrected" ash see the preliminary report.<sup>8</sup> The actual mineral matter in the original coal is usually very different in weight and composition from the weight of the "uncorrected" ash.

NOTE 7.—Difficulty may be experienced in securing satisfactory check determinations of ash in the same or different laboratories for coals unusually high in calcite and pyrite. This is caused by varying amounts of sulfate sulfur being retained in the ash. When such difficulty is encountered, or when coals of relatively high ash content whose mineral matter composition is unknown are encountered, the ash should be determined by the following modified procedures:

(a) Place the porcelain capsules containing the dried coal from the moisture determination in a cold muffle furnace and heat gradually so that the temperature reaches 500°C. in 1 hour, and 750°C. in 2 hours. Heat to constant weight at 750°C. By this means pyritic sulfur will be oxidized and expelled before the calcite is decomposed. An ample supply of air in the muffle must be assured at all times to ensure complete oxidation of the pyritic sulfur and proper circulation through the muffle must be assured to remove the  $\text{SO}_3$  formed.

(b) The modified procedure described in paragraph (a) should be adequate for determining ash in all troublesome commercial samples. However, samples may be encountered in certain special studies whose ash values are quite high and whose mineral matter contains much greater than normal amounts of calcite and pyrite. In such cases sulfate sulfur should be determined on the ash obtained by the modified cold muffle method and the value properly corrected, or the Parr<sup>9</sup> sulfated ash method as modified by Rees<sup>10</sup> should be used.

**15. Procedure for Coke.**—Place the capsules containing the dried coke from the moisture determination in a muffle furnace or over a burner, and heat to redness at such a rate as to avoid mechanical loss (Note 5). Finish the ignition to constant weight ( $\pm 0.001$  g.) at a temperature not exceeding 950°C. Cool in a desiccator, and weigh.

NOTE 8.—Test the ash for unburned carbon by moistening it with alcohol; any carbon remaining will show as black particles.

### VOLATILE MATTER

**16. Apparatus.** Platinum Crucible with Closely Fitting Cover, for Coal.—The crucible shall be of not less than 10 nor more than 20 ml. in capacity, not less than 25 nor more than 35 mm. in diameter, and not less than 30 nor more than 35 mm. in height.

Platinum Crucible with Closely Fitting Cover, for Coke.—The crucible shall be of 10-ml. capacity, with capsule cover having thin flexible sides fitting down into crucible. Or the double-crucible method may be used, in which the sample is placed in a 10- or 20-ml. platinum crucible, which is then covered with another crucible of such a size that it will fit closely to the sides of the outer crucible, and its bottom will rest  $\frac{1}{8}$  to  $\frac{1}{2}$  in. above the bottom of the outer crucible.

Vertical Electric Tube Furnace, or a Gas or Electrically Heated Muffle Furnace, for Coal or Coke.—The furnace may be of the form shown in Fig. 31-7. It shall

<sup>8</sup> Report on Fixed Carbon and Ash, *Proceedings*, Am. Soc. for Testing Mats., Vol. XIV, Part I, p. 426 (1914).

<sup>9</sup> S. W. Parr, "Chemical Study of Illinois Coal," *Bulletin No. 3*, p. 35, Illinois Coal Mining Investigations, State Geological Survey, Urbana, Ill. (1916).

<sup>10</sup> O. W. Rees, "Determining Ash in High Carbonate Coals. Study of the Modified Method," *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 9, pp. 307-309 (1937).

case of coke, after heating 2 or 3 minutes, tap the cover lightly to more perfectly seal the crucible and thus guard against the admission of air. After heating for exactly 7 minutes, remove the crucible from the furnace and, without disturbing the cover, allow it to cool. Coke should be cooled in a desiccator. Weigh as soon as cold. The loss of weight minus moisture equals the volatile matter.

NOTE 9.—The cover should fit closely enough so that the carbon deposit from bituminous, subbituminous, and lignitic coals does not burn away from the under side.

NOTE 10.—Regulation of temperature to within the prescribed limits is important.

NOTE 11.—With some strongly caking low-volatile and medium-volatile bituminous coals, the coke button may be broken with explosive violence, due to the liberation of volatile matter within the button. This is usually designated as "popping." Such popping may blow the lid off the crucible and cause mechanical losses of the coked material. When such popping is observed, the determination shall be rejected and the test repeated until popping does not occur.

**18. Modified Procedure for Subbituminous Coal, Lignite, Peat, and Certain Cokes, Chars, Anthracites, and Semianthracites.**—(a) Mechanical losses are incurred on suddenly heating peat, lignite, and subbituminous coal; such losses also occur with some low-temperature cokes, green cokes, chars, anthracites, and semianthracites. This mechanical loss is usually designated as "sparking" and is caused by particles of the fuel being ejected from the crucible by the too rapid escape of steam or volatile matter. These particles become incandescent in the flame of the burning volatile constituents and may be seen around the edge of the crucible cover, sometimes only  $\frac{1}{4}$  in. above the crucible and at other times shooting several inches to the top of the furnace. In severe cases of sparking, ash deposits and sometimes unburned material will be found on the crucible cover. Small amounts of ash deposits are sometimes found on the crucible cover in case of moderately sparking fuels. All fuels that do not cake when volatile matter is determined shall be watched closely for sparking during the heating period; also, at the end of the test the crucible cover shall be inspected for ash deposits, and the presence of such deposits shall be considered as evidence of sparking.

(b) **Volatile Matter by Modified Procedure.**—All fuels that spark when the volatile matter is determined by the methods described in Sections 17 and 19 shall be treated as follows: The sample shall be given a preliminary gradual heating such that a temperature of  $600^{\circ} \pm 50^{\circ}\text{C.}$  is reached in 6 minutes (Notes 12, 13, 14). After this preliminary heating the sample is heated for exactly 6 minutes at  $950^{\circ} \pm 20^{\circ}\text{C.}$  If sparking is then observed the determination shall be rejected and the test repeated until no sparking occurs either during the preliminary heating or during the 6-minute period at  $950^{\circ}\text{C.}$  Remove crucible from furnace and cool on a metal cooling block and weigh (Note 15). The percentage loss in weight minus the per cent moisture is the volatile matter. All analyses by this method shall be marked to indicate that the modified procedure was used.

NOTE 12.—If a tubular furnace of the Fieldner type is used for the determination of volatile matter, the preliminary gradual heating may be accomplished by moving the crucible to predetermined positions in the cooler top zone of the furnace. Due to variations in the heating characteristics of the furnace, the operator must determine by the thermocouple method in Section 19 for each furnace the proper position to meet preliminary heating rate as specified. It is also possible to use a mechanical device to lower the crucible into the furnace.

NOTE 13.—If electric muffle furnaces are used the heating may be accomplished by using two furnaces situated side by side, one furnace being controlled at  $550^{\circ} \pm 10^{\circ}\text{C.}$ , the other at  $950^{\circ} \pm 10^{\circ}\text{C.}$  The crucible containing the sample is placed on a Nichrome support  $\frac{3}{8}$  to  $\frac{1}{2}$  in. high, and placed in the muffle furnace controlled at  $550^{\circ} \pm 10^{\circ}\text{C.}$  for exactly 6 minutes, after which time it is rapidly transferred along with its Nichrome support to the second muffle furnace, controlled at  $950^{\circ} \pm 10^{\circ}\text{C.}$ , and allowed to remain for exactly 6 minutes.

NOTE 14.—If the Meker burner method described in paragraph (c) is used, the rate of heating specified in (b) shall be observed.

NOTE 15.—To insure uniformity of results the cooling period should be kept constant and should not be prolonged beyond 15 minutes.

(c) If the Meker burner method described in Section 19 is used for the volatile matter determination, the preliminary heating shall be done by playing the flame of a burner upon the bottom of the crucible in such a manner as to bring about the discharge of volatile matter at a rate not sufficient to cause sparking. After this preliminary heating, the crucible shall be heated for exactly 6 minutes at  $950^{\circ}\text{C.}$  as described in Section 19. If sparking occurs during this 6-minute heating period, the determination shall be rejected and another made.

19. *Procedure for Coal and Coke, Using Meker Burner.*—Weigh 1 g. of the sample in a weighed platinum crucible and close with a cover or, in the case of coke, another crucible as described in Section 16. Place in the flame of a No. 4 Meker burner, having an outside diameter at the top of approximately 25 mm. and giving a flame not less than 15 cm. in height. The temperature should be  $950^{\circ} \pm 20^{\circ}\text{C.}$  as determined by placing a thermocouple through the perforated cover, which for this purpose may be of nickel or asbestos. The junction of the couple should be placed in contact with the center of the bottom of the crucible; or the temperature may be indicated by the fusion of pure potassium chromate ( $\text{K}_2\text{CrO}_4$ ) in the covered crucible (fusion of  $\text{K}_2\text{CrO}_4$ ,  $968^{\circ}\text{C.}$ ).<sup>11</sup> The crucible shall be placed in the flame about 1 cm. above the top of the burner and the heating continued 7 minutes. Where the gas pressure is variable it is well to use a U-tube attachment to the burner.

### FIXED CARBON

20. Calculation.—Calculate fixed carbon in coal or coke, as follows:

$$\text{Fixed carbon, \%} = 100 - (\text{moisture} + \text{ash} + \text{volatile matter})$$

### SULFUR BY THE ESCHKA METHOD

21. *Apparatus.* Gas or electric muffle furnace, or burners, for igniting the sample with the Eschka mixture and for igniting the barium sulfate ( $\text{BaSO}_4$ ).

Crucibles or Capsules.—Porcelain capsules,  $\frac{7}{8}$  in. in depth and  $1\frac{1}{4}$  in. in diameter, or porcelain crucibles of 30-ml. capacity, high or low form, or platinum crucibles of similar size shall be used for igniting the sample with the Eschka mixture. Porcelain, platinum, alundum, or silica crucibles of 10- to 15-ml. capacity, shall be used for igniting the  $\text{BaSO}_4$ .

22. *Reagents.* Barium Chloride Solution (100 g. per liter).—Dissolve 100 g. of barium chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) in 1 liter of water.

Bromine Water (Saturated).—Add an excess of bromine to 1 liter of water.

<sup>11</sup> U. S. Bureau of Mines, *Reports of Investigations*, Serial No. 2917 (1929).

**Eschka Mixture.**—Thoroughly mix 2 parts by weight of light calcined magnesium oxide ( $\text{MgO}$ ) with 1 part of anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). Both materials should be as free as possible from sulfur.

**Hydrochloric Acid (1:1).**—Mix equal volumes of concentrated hydrochloric acid ( $\text{HCl}$ , sp. gr. 1.19) and water.

**Hydrochloric Acid (1:9).**—Mix 1 volume of concentrated hydrochloric acid ( $\text{HCl}$ , sp. gr. 1.19) with 9 volumes of water.

**Methyl Orange Indicator Solution (0.2 g. per liter).**—Dissolve 0.02 g. of methyl orange in 100 ml. of hot water and filter.

**Sodium Carbonate, Saturated Solution.**—Dissolve approximately 60 g. of crystallized sodium carbonate ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) or 22 g. of anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in 100 ml. of water, using a sufficient excess of  $\text{Na}_2\text{CO}_3$  to insure a saturated solution.

**Sodium Hydroxide Solution (100 g. per liter).**—Dissolve 100 g. of sodium hydroxide ( $\text{NaOH}$ ) in 1 liter of water. This solution may be used in place of the  $\text{Na}_2\text{CO}_3$  solution.

**23. Procedure for Coal and Coke.** (a) **Preparation of Sample and Mixture.**—Thoroughly mix on glazed paper approximately 1 g. of the sample and 3 g. of Eschka mixture. The amount of sample to be taken will depend on the amount of  $\text{BaCl}_2$  solution required in accordance with paragraph (c). Transfer to a porcelain capsule or porcelain crucible, or a platinum crucible, and cover with about 1 g. of Eschka mixture.

(b) **Ignition.**—On account of the amount of sulfur contained in artificial gas, the crucible shall be heated over an alcohol, gasoline, or natural gas flame as described in Item (1) of this paragraph, or in a gas or electrically heated muffle as described in Item (2) for coal and in Item (3) for coke. The use of artificial gas for heating the sample and Eschka mixture is permissible only when the crucibles are heated in a muffle.

(1) Heat the crucible, placed in a slanting position on a triangle, over a very low flame to avoid rapid expulsion of the volatile matter which tends to prevent complete absorption of the products of combustion of the sulfur. Heat the crucible slowly for 30 minutes, gradually increasing the temperature and stirring after all black particles have disappeared, which is an indication of the completeness of the procedure.

(2) **For Coal.** Place the crucible in a cold muffle and gradually raise the temperature to  $800^\circ \pm 25^\circ\text{C}$ . in about 1 hour. Maintain this maximum temperature for about  $1\frac{1}{2}$  hours.

(3) **For Coke.** Place the crucible in a warm muffle and gradually raise the temperature to  $800^\circ \pm 25^\circ\text{C}$ . in about 30 minutes. Maintain this maximum temperature until on stirring all black particles have disappeared.

(c) **Subsequent Treatment.**—Remove the crucible and empty the contents into a 200-ml. beaker and digest with 100 ml. of hot water for  $\frac{1}{2}$  to  $\frac{3}{4}$  hour, while stirring occasionally. Filter and wash the insoluble matter by decantation. After several washings in this manner, transfer the insoluble matter to the filter and wash five times, keeping the mixture well agitated. Treat the filtrate, amounting to about 250 ml., with 10 to 20 ml. of saturated bromine water, make slightly acid with  $\text{HCl}$ , and boil to expel the liberated bromine. Make just neutral to methyl orange with  $\text{NaOH}$  or  $\text{Na}_2\text{CO}_3$  solution; then add 1 ml. of  $\text{HCl}$  (1:9). Boil again and add slowly from a pipet, while stirring constantly, 10 ml. or more of  $\text{BaCl}_2$  solution. The  $\text{BaCl}_2$  solution must be in excess. Whenever more than 10 ml. of  $\text{BaCl}_2$  solu-



tion is required, the weight of sample (paragraph (a)) shall be reduced to about 0.5 g. depending on the sulfur content. Continue boiling for 15 minutes and allow to stand for at least 2 hours, or preferably overnight, at a temperature just below boiling. Filter through an ashless paper and wash with hot water until silver nitrate ( $\text{AgNO}_3$ ) solution shows no precipitate with a drop of the filtrate.

Place the wet filter containing the precipitate of barium sulfate ( $\text{BaSO}_4$ ) in a weighed platinum, porcelain, silica, or alundum crucible, allowing a free access of air by folding the paper over the precipitate loosely to prevent spattering. Smoke the paper off gradually and at no time allow it to burn with flame. After the paper is practically consumed, raise the temperature to approximately  $925^\circ\text{C}$ . and heat to constant weight.

Dissolve the residue of magnesium oxide ( $\text{MgO}$ ), etc., after leaching, in  $\text{HCl}$  and test with great care for sulfur. When an appreciable amount is found this should be determined quantitatively. The amount of sulfur retained is by no means a negligible quantity.<sup>12</sup>

(d) **Blanks and Corrections.**—In all cases, a correction must be applied either by running a blank exactly as described above, using the same amount of all reagents that were employed in the regular determination, or more accurately by determining a known amount of sulfate added to a solution of the reagents after these have been put through the prescribed series of operations. If this latter procedure is adopted and carried out once a week or whenever a new supply of a reagent must be used, and for a series of solutions covering the range of sulfur content likely to be met with in the samples, it is only necessary to add to or subtract from the weight of  $\text{BaSO}_4$  obtained from a sample, whatever deficiency or excess may have been found in the appropriate "check" in order to obtain a result that is more certain to be correct than if a "blank" correction as determined by the former procedure is applied. This is due to the fact that the solubility error for  $\text{BaSO}_4$ , for the amounts of sulfur in question and the conditions of precipitation prescribed, is probably the largest one to be considered. Barium sulfate is soluble<sup>13</sup> in acids and even in pure water, and the solubility limit is reached almost immediately on contact with the solvent. Hence, in the event of using reagents of very superior quality, or of exercising more than ordinary precautions, there may be no apparent "blank" because the solubility limit for the solution for  $\text{BaSO}_4$  has not been reached or at any rate not exceeded.

24. **Calculation.**—Calculate the sulfur content as follows:

$$\text{Sulfur, \%} = \frac{(A - B) \times 13.735}{C}$$

where  $A$  = grams of  $\text{BaSO}_4$  precipitated

$B$  = grams of  $\text{BaSO}_4$  in the blank

$C$  = grams of sample used

NOTE 16.—As shown in the preliminary report,<sup>14</sup> the Atkinson and sodium peroxide methods give results in close agreement with the Eschka method. Regester<sup>15</sup> has shown that if 5% of nitrogen is present in the gases contained in the bomb calorimeter the sulfur of a sample is almost completely oxidized to sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and the washings of the calorimeter may be used for the determination of sulfur.

<sup>12</sup> *Journal, Am. Chem. Soc.*, Vol. 21, p. 1125 (1899).

<sup>13</sup> *Journal, Am. Chem. Soc.*, Vol. 32, p. 588 (1910). Vol. 33, p. 829 (1911).

<sup>14</sup> *Journal of Industrial and Engineering Chemistry*, Vol. 5, p. 5 (1913).

<sup>15</sup> *Ibid.*, Vol. 6, p. 812 (1914).

*SULFUR BY THE BOMB WASHING METHOD*<sup>16</sup>

**25. Reagents.** Ammonium Hydroxide (sp. gr. 0.90).—Concentrated ammonium hydroxide ( $\text{NH}_4\text{OH}$ ).

Bromine Water (Saturated).—See Section 22.

Hydrochloric Acid (1:1).—See Section 22.

Sodium or Potassium Hydroxide, Standard Solution.

Wash Solution.—Dilute 1 ml. of a saturated solution of methyl orange to 1 liter with water.

**26. Procedure for Coal and Coke.** Ignition.—Sulfur is determined in the washings from the oxygen-bomb calorimeter following the calorimetric determination. The type of bomb, amount of water in the bomb, oxygen pressure, and amount of sample taken shall be the same as specified under the calorimetric determination (see Sections 51 to 54 of ASTM D271-58 not included here). The bomb shall stand in the calorimeter water for not less than 5 minutes after firing.

Subsequent Treatment.—Remove the bomb from the calorimeter water and open the valve carefully so as to allow the gases to escape at an approximately even rate so the pressure is reduced to atmospheric in not less than 1 minute. Bombs equipped with valves other than needle valves, such as compression valves, shall be provided with a device so the valve can be controlled to permit a slow and uniform release of the gases. Open the bomb and examine the inside for traces of unburned material or sooty deposit. If these are found, the determination shall be discarded. Wash carefully all parts of the interior of the bomb, including the tray, with a fine jet of water containing methyl orange (see Section 25) until no acid reaction is observed. It is essential to wash through the valve opening in the case of bombs equipped with compression valves, or other types of valves with large openings, as considerable spray may collect in such valve openings.

Collect the washings in a 250-ml. beaker and titrate with standard sodium or potassium hydroxide solution to obtain the "acid correction" for the heating value, as specified under the calorimetric determination. Add 1 ml. of  $\text{NH}_4\text{OH}$ , heat the solution to boiling, and filter through a qualitative paper. Wash the residue and paper thoroughly five or six times with hot water. To the filtrate and washings, amounting to about 250 ml., add 1 ml. of saturated bromine water and sufficient  $\text{HCl}$  to make it slightly acid. Boil the solution to expel the excess bromine. Adjust the acidity, precipitate, and determine the sulfur as specified under the Eschka method, Section 23.

*SULFUR BY THE SODIUM PEROXIDE FUSION METHOD*<sup>16</sup>

**27. Apparatus.** Combustion Bomb.—The Parr coal-sulfur bomb, or its equivalent, shall be used. The bomb shall have an inner surface that is not attacked by the chemicals on ignition of the charge.

**28. Reagents.** Benzoic acid, powdered.

Hydrochloric Acid (sp. gr. 1.19).—Concentrated hydrochloric acid ( $\text{HCl}$ ).

Potassium chlorate ( $\text{KClO}_3$ ), powdered.

Potassium perchlorate ( $\text{KClO}_4$ ), powdered.

Sodium peroxide ( $\text{Na}_2\text{O}_2$ ), powdered, sulfur-free.

**29. Procedure for Coal and Coke.**—Place 1 g. of  $\text{KClO}_4$  or  $\text{KClO}_3$  in a dry sulfur

<sup>16</sup> W. A. Selvig and A. C. Fieldner, "Check Determinations of Sulfur in Coal and Coke by the Eschka, Bomb-Washing, and Sodium Peroxide Fusion Methods," *Industrial and Engineering Chemistry*, Vol. 29, pp. 729-733 (1927).

bomb and break up any lumps that occur. Add 0.5 g. of the sample and mix thoroughly with a glass rod. Then add about 15 g. of  $\text{Na}_2\text{O}_2$  (Caution, Note 17) close the bomb, and mix thoroughly by shaking. In the case of cokes or anthracites, or coals excessively high in ash that fail to ignite or fuse properly (as indicated by the fusion being honeycombed in appearance), add 0.3 g. of benzoic acid to the bomb at the time the chlorate and sample are added.

NOTE 17: Caution.—It should be noted that a mixture of  $\text{KClO}_3$  and organic matter alone produces a mixture of extremely explosive properties. One of the important functions of the  $\text{Na}_2\text{O}_2$  is to provide a diluent, thus slowing down the reaction, so care should be taken that it is not omitted in the charge. Potassium perchlorate is fully equal if not superior to the  $\text{KClO}_3$ , and is without turbulence in its reaction.

Fasten the cover securely to the bomb and ignite the charge (Caution, Note 18) by applying a sharply pointed flame from a blast lamp to the bottom of the bomb for a brief period, or by electric ignition, according to the type of bomb used. Allow 1 minute for complete combustion to take place after ignition; then cool under the tap or in a vessel of water.

NOTE 18: Caution.—Place the bomb inside a piece of steel pipe when the charge is ignited to prevent possible injury to the operator if the bomb should burst.

Remove the cover from the bomb, place the bomb on its side in a 400-ml. beaker, and wash the cover with a fine jet of hot water. Place a watch glass over the beaker and cautiously add about 100 ml. of hot water. After the contents of the bomb have dissolved, remove and rinse it carefully with the water. Slowly add  $\text{HCl}$  to the neutral point; then add 1 to 2 ml. of  $\text{HCl}$  in excess. Filter through qualitative paper into a 600-ml. beaker and wash thoroughly five or six times with water. Dilute the filtrate to approximately 400 ml., and precipitate the sulfur with  $\text{BaCl}_2$  solution and determine as specified under the Eschka method, Section 23.

Blank Correction.—Apply a correction by running a blank on the reagents used.

### PHOSPHORUS IN ASH

30. *Reagents.* Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ).

Hydrofluoric acid ( $\text{HF}$ ).

Molybdate Solution.—Dissolve 65 g. of molybdic acid (85%  $\text{MoO}_3$ ) in a mixture of 143 ml. of  $\text{NH}_4\text{OH}$  and 142 ml. of water. Add this solution slowly, while stirring constantly, to 715 ml. of  $\text{HNO}_3$  (3:5). If the solution is cloudy, add two drops of the ammonium phosphate solution and allow the precipitate which forms to settle. Filter the solution into bottles and, if necessary, refilter just before using. If the molybdic acid used is 100%  $\text{MoO}_3$ , 56 g. should be taken instead of 65 g.

Nitric Acid (sp. gr. 1.42).—Concentrated nitric acid ( $\text{HNO}_3$ ).

Nitric Acid (3:5).—Mix 3 volumes of  $\text{HNO}_3$  (sp. gr. 1.42) with 5 volumes of water.

Potassium nitrate ( $\text{KNO}_3$ ).

Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ).

Sodium Hydroxide, Standard Solution.—The sodium hydroxide ( $\text{NaOH}$ ) may well be made equal to 0.00025 g. of phosphorus per milliliter, or 0.005% for a 5-g. sample. Such a solution would be 0.926 of 0.2 N.<sup>17</sup>

Sodium nitrate ( $\text{NaNO}_3$ ).

31. *Procedure for Coal and Coke: For all Cases.*—Add to the ash from 5 g. of the sample, in a platinum crucible, 10 ml. of  $\text{HNO}_3$  (sp. gr. 1.42) and 3 to 5 ml. of  $\text{HF}$ .

<sup>17</sup> Ulman and Buch, *Chemical Engineer*, Vol. 10, p. 130 (1909).

Evaporate the liquid, ignite the residue, and fuse with 3 g. of  $\text{Na}_2\text{CO}_3$ . If unburned carbon is present, mix 0.2 g. of  $\text{NaNO}_3$  with the carbonate. Leach the melt with water and filter the solution.

Ignite the residue, fuse with  $\text{Na}_2\text{CO}_3$  alone, leach the melt with water, and filter the solution. Just acidify with  $\text{HNO}_3$  the combined filtrate held in a flask, add 3 to 5 ml. of  $\text{HNO}_3$  (sp. gr. 1.42) in excess, and concentrate to a volume of 100 ml.

Add 6 g. of  $\text{NH}_4\text{NO}_3$ , bring the temperature of the solution to  $80^\circ\text{C}$ ., add 50 ml. of molybdate solution, and shake the flask for 10 minutes. When the precipitate has settled, filter, and wash the precipitate until free from acid with  $\text{KNO}_3$  solution (2%).

Place the filter paper with the precipitate in the flask, add 25 ml. of recently boiled water, and macerate the filter paper with a glass stirring rod. Add a measured excess of  $\text{NaOH}$  solution and agitate the solution to completely dissolve the precipitate. Add three drops of phenolphthalein solution as an indicator and titrate the excess  $\text{NaOH}$  with a standard  $\text{HNO}_3$  solution.

NOTE 19.—The advantage of the use of  $\text{HF}$  in the initial attack of the ash lies in the resulting removal of silica. Fusion with alkali carbonate is necessary for the elimination of titanium, which if present and not removed will contaminate the phosphomolybdate and is said to sometimes retard its precipitation.

**32. Procedure for Coal and Coke: When Titanium Is Low.**—When titanium is so low as to offer no interference, decompose the ash as described in Section 31, but carry the evaporation only to a volume of about 5 ml. Dilute the solution with water to 30 ml., boil, and filter into a flask. If the washings are turbid, pass them again through the filter. Ignite the residue in a platinum crucible, fuse with a small amount of  $\text{Na}_2\text{CO}_3$ , dissolve the melt in  $\text{HNO}_3$ , and add the solution, if clear, to the main one. If not clear, filter. The fusion of the residue may be dispensed with in routine work on a given coal or coke, if it is certain that the residue is free from phosphorus.

Add  $\text{NH}_4\text{OH}$  to the filtrate until a slight precipitate ensues. Add  $\text{HNO}_3$  (sp. gr. 1.42) to just dissolve the precipitate; then add 3 to 5 ml. of the acid in excess. Heat the solution, which should have a volume of about 100 ml., to  $80^\circ\text{C}$ . and add 50 ml. of molybdate solution. Shake the flask for 10 minutes, filter and determine the phosphorus as described in Section 31.

### CARBON AND HYDROGEN

**33.** The determination of carbon and hydrogen is made by burning a weighed quantity of sample in a closed system and fixing the products of combustion in an absorption train after complete oxidation and purification from interfering substances. This method gives the total percentages of carbon and hydrogen in the coal as analyzed, and includes the carbon in carbonates and the hydrogen in the moisture and in the water of hydration of silicates.

**34. Apparatus.** Oxygen purifying train, consisting of the following units arranged as listed in the order of passage of oxygen.

(1) *First Water Absorber.* A container for the solid dehydrating reagent. It shall be so constructed that the oxygen must pass through a column of reagent adequate to secure water equilibrium equal to that secured in the prescribed absorption train. A container of large volume and long path of oxygen travel through the reagent will be found to be advantageous where many carbon and hydrogen determinations are made.

(2) *Carbon Dioxide Absorber.* A container for solid carbon dioxide absorbing agent. It shall be constructed as described in item (1) (above) and shall provide for a column of reagent adequate to remove completely carbon dioxide.

(3) *Second water absorber*, same as specified in Item (1) of this paragraph.

(4) *Flow meter*, used to permit volumetric measurement of the rate of flow of oxygen during the determination. It shall be suitable for measuring flow rates within the range of 50 to 100 ml. per minute (standard temperature and pressure). The use of a double-stage pressure-reducing regulator with gauge and needle valve preceding the first water absorber is recommended to permit easy and accurate adjustment of the rate of flow.

**Combustion Unit.**—The combustion unit shall consist of three electrically heated furnace sections, individually controlled, which may be mounted on rails for easy movement; the upper part of each furnace may be hinged so that it can be opened for inspection of the combustion tube. The three furnace sections shall be as follows:

(1) *Furnace Section 1*, nearest the oxygen inlet end of the combustion tube, approximately 13 cm. long and used to heat the inlet end of the combustion tube and the sample. It shall be capable of rapidly attaining an operating temperature of  $850^{\circ}$  to  $900^{\circ}\text{C}$ . (Note 20).

(2) *Furnace Section 2*, approximately 33 cm. in length and used to heat that portion of the tube filled with cupric oxide. The operating temperature shall be  $850^{\circ} \pm 20^{\circ}\text{C}$ . (Note 20).

(3) *Furnace Section 3*, approximately 23 cm. long, and used to heat that portion of the tube filled with lead chromate or silver. The operating temperature shall be  $500^{\circ} \pm 50^{\circ}\text{C}$ . (Note 20).

NOTE 20.—Combustion tube temperatures shall be measured by means of a thermocouple placed immediately adjacent to the tube near the center of the appropriate tube section.

**Combustion Tube.**—The combustion tube shall be made of fused quartz or high-silica glass<sup>18</sup> and shall have a nominal inside diameter which may vary within the limits of 19 to 22 mm. and a minimum total length of 97 cm. The exit end shall be tapered down to provide a tubulated section for connection to the absorption train. The tubulated section shall have a length of 2 to 2.5 cm., an internal diameter of not less than 3 mm., and an external diameter of approximately 7 mm. The total length of the reduced end shall not exceed 6 cm. If a translucent fused quartz tube is used, a transparent section 10 cm. long, located 25 cm. from the oxygen inlet end of the tube, will be found convenient.

**Combustion Boat.**—This shall be either glazed porcelain, fused silica, or platinum. Boats with internal dimensions of approximately 70 by 8 by 8 mm. have been found convenient.

**Absorption Train.**—The absorption train shall consist of the following units arranged as listed in the order of passage of oxygen:

(1) *Water absorber*, having a capacity for 45 cu. cm. of solid reagent and a minimum length of gas travel through the reagent of 8 cm.<sup>19</sup>

(2) *Carbon Dioxide Absorber.* If solid reagents are used for carbon dioxide absorption the container shall be as described in Item (1) of this paragraph. If a solution is used, the container shall be a Vanier bulb.

<sup>18</sup> Vycor has been found satisfactory for this purpose.

<sup>19</sup> Glass-stoppered containers such as the Nesbitt, Schwartz U-tube and the Stetser-Norton bulb have been found satisfactory.

(3) *Guard Tube.* A container as described in Item (1) of this paragraph.

35. *Reagents.* Oxygen, 99.5% purity or better (Note 24).

*Combustion Tube Reagents.*—(1) *Cupric oxide*, (CuO) wire form, dust-free.

(2) *Lead chromate*, (PbCrO<sub>4</sub>) approximately 8- to 20-mesh size.

(3) *Silver gauze*, 99.9% silver minimum purity, 20 mesh, made from approximately No. 27 B. & S. gauge wire.

(4) *Copper gauze*, 99.0% copper minimum purity, 20 mesh made from approximately No. 26 B. & S. gauge wire.

*Purification and Absorption Train Reagents.*—(1) *Water Absorbent.* Anhydrous magnesium perchlorate (Mg(ClO<sub>4</sub>)<sub>2</sub>) of approximately 8- to 45-mesh size (Note 21).

NOTE 21.—Trade names of the reagents are Anhydrone and Dehydrite.

(2) *Carbon Dioxide Absorbent.* If a solid reagent is used, it shall be sodium or potassium hydroxide (NaOH or KOH) impregnated in an inert carrier of approximately 8- to 20-mesh size. Use of soda lime in place of the above or in admixture with them is permissible (Note 22). If a solution is used, it shall be 30% by weight potassium hydroxide (KOH).

NOTE 22.—Trade names of the sodium and potassium hydroxide permissible solid carbon dioxide absorbing reagents are: Ascarite, Caroxite, and Mikohbite. If soda lime is used in admixture with any of the foregoing, it should not exceed 30% by weight of the total reagent. In using Ascarite it may be necessary to add a few drops of water to this reagent to assure complete absorption of carbon dioxide.

36. *Preparation of Apparatus.* *Combustion Tube Packing.*—To ensure complete oxidation of combustion products and complete removal of interfering substances such as oxides of sulfur, the combustion tube shall be packed with cupric oxide

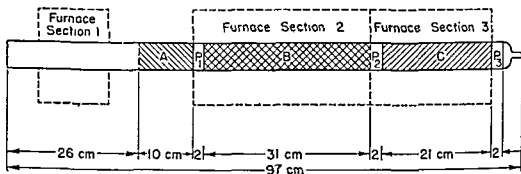


FIG. 31-8. Arrangement of Tube Fillings for Combustion Tube.

A—Clear fused quartz section (optional) when a translucent quartz tube is used.

B—Cupric oxide filling.

C—Lead chromate or silver filling.

P<sub>1</sub>, P<sub>2</sub>, or P<sub>3</sub>—oxidized copper gauze plugs.

NOTE.—All dimensions are given in centimeters. When furnace sections longer than those specified in Section 34 are to be used, changes in the above dimensions shall be in accordance with the provisions of Note 23.

and lead chromate or silver. The arrangement and lengths of the tube fillings and separating plugs shall be as shown in Fig. 31-8. It is recommended that the tube be placed in a vertical position (constricted end downward) for packing. When filling the tube with lead chromate, any residual reagent adhering to the walls of

the empty portion of the tube must be removed. When silver is used as a tube filling, the required length of filling may be prepared conveniently from three or four strips of silver gauze 15 to 20 cm. long, by rolling each strip into a cylindrical plug and inserting the strips end-to-end in the tube (Note 23).

NOTE 23.—Longer furnaces with appropriate lengths of tube packing will be satisfactory.

**Absorption Train.**—(1) *Water absorber*, consisting of a container filled with a permissible solid desiccant by adding the required amount in small portions and settling each portion by gentle tapping between additions. A glass wool plug shall be placed between the reagent and the absorber outlet to prevent loss of reagent "dust."

(2) *Carbon Dioxide Absorber*. If a solid reagent is used for the retention of carbon dioxide, the absorber shall be filled as described in Item (1) of this paragraph. A layer or "cap" of desiccant shall be placed in the outlet section of the container and shall be the same as that used in the water absorber. This layer shall have a bulk volume not less than one-fourth nor more than one-third of the combined volume of both reagents. If a liquid absorbent is used, the inner tube of the Vanier bulb shall be filled with the same desiccant used in the water absorber. A glass wool plug shall be placed in the outlet section of the container to prevent loss of reagent "dust."

(3) *Guard tube*, packed with equal volumes of the water absorbent and a solid carbon dioxide absorbent.

**Connections.**—To ensure a closed system from the supply tank of oxygen to the guard tube at the end of the absorption train, it is recommended that all connections be glass-to-glass or glass-to-quartz butt joints with short lengths of flexible tubing as seals. The connection between the purification train and the combustion tube may be made by means of a rubber stopper or other suitable device. All connections shall be gas-tight. No lubricant shall be used for making tubing connections in the absorption train.

**Conditioning of Apparatus.**—(1) *Newly Packed Combustion Tube*. A sample of coal or coke shall be burned as described in Section 37, except that the products of combustion need not be fixed in a weighed absorption train.

(2) *Used Combustion Tube*. After any extended shut down, one day or more, the combustion train shall be tested under procedure conditions, but without burning a sample, for 40 minutes with weighed absorption bulbs connected. A variation of not more than 0.5 mg. of either bulb shall be considered satisfactory (Note 24).

NOTE 24.—If the blank tests for flow indicate interfering impurities in the oxygen supply by consistent weight-gain in the absorption bulbs, these impurities shall be eliminated by using a preheater furnace and tube, filled with cupric oxide. This preheater furnace shall be operated at  $850^{\circ} \pm 20^{\circ}\text{C}$ . and shall be inserted in series between the supply tank of oxygen and the purification train.

(3) *Absorption Train*. Freshly packed absorber and guard tubes shall be conditioned by burning a sample of coal or coke as described in Section 37, except that tube weights need not be determined.

(4) *Standard checks* shall be made frequently, particularly when intermittent use of the combustion train is common or when any changes have been made in the system. A standard substance of certified analysis, such as benzoic acid or sucrose

as furnished by the National Bureau of Standards shall be burned as described in Section 37. A variation from the theoretical of not more than 0.07% for hydrogen nor more than 0.30% for carbon shall be considered satisfactory.

**37. Procedure.**—After the combustion tube and absorbers have been conditioned as prescribed in Section 36, the test shall be made as follows:

(a) **Absorption Train.**—Bring the absorption tubes to room temperature near the balance for 15 to 20 minutes, vent momentarily to the atmosphere, wipe with a chamois or lint-free cloth in the areas where handled, and weigh to the nearest 0.1 mg.

(b) **Sample.**—Weigh approximately 0.2 g. (weighed to the nearest 0.1 mg.) of air-dry sample ground to pass a No. 60 (250 micron) sieve into a combustion boat (Note 25).

(c) **Sample Analysis.**—With furnace Sections 2 and 3 at specified temperatures and positioned as shown in Fig. 31-8, perform the following operations in rapid succession in the order listed:

(1) If a conventional type of sample heating furnace is used for heating section No. 1, place it so that its left-hand edge is about 10 cm. from the oxygen inlet end of the combustion tube.

(2) Attach the weighed absorption train to the tube.

(3) Push the sample boat into the tube to a point within approximately 2 cm. from plug  $P_1$ .

(4) Close the tube and adjust the oxygen flow to a rate of 50 to 100 ml. per minute (standard temperature and pressure) being the same as used in blanking, Section 36 for Used Combustion Tube.

(5) Apply full heat to heating section No. 1 to bring it to an operating temperature of 850° to 900°C. as rapidly as possible.

Move the heater slowly toward the boat so that it completely covers the boat and is brought into contact with heating section No. 2 in a period of 10 to 20 minutes (Note 26). Allow it to remain in this position for an additional 5 to 10 minutes, and then shut off the heat and return the sample heater to its original position. Continue the flow of oxygen through the tube for 10 minutes (Note 27), close the absorbers under a positive pressure of oxygen, and detach them from the train. Remove the absorbers to the vicinity of the balance, allow them to cool to room temperature for 15 to 20 minutes, vent momentarily to atmosphere, wipe them with a chamois or lint-free cloth in the areas handled, and finally weigh them to the nearest 0.1 mg. While the absorbers are cooling, it is recommended that the ash remaining in the combustion boat be examined for traces of unburned carbon which, if present, will nullify the determination.

**NOTE 25.**—It may be beneficial to grind fly ash, pit ash, calcined coke, and high mineral content materials to pass a No. 100 (149 micron) sieve.

**NOTE 26.**—Some variation in operating technique and heater manipulation may be permitted here at the discretion of the analyst, provided that is conducive to a gradual and controlled release of volatile matter. Conditions that lead to visible burning (flame combustion) of the sample shall be avoided.

**NOTE 27.**—Since water may condense in the cooler outlet end of the combustion tube or in the inlet arm of the water absorber, the use of an external or internal heat conducting device (a metal heat bridge) is recommended to prevent such condensation or promote re-evaporation during this flushing period.

**38. Calculations.**—Calculate the percentage of carbon (Note 28) and hydrogen as follows:



$$\text{Hydrogen, \%} = \frac{A \times 11.190}{C}$$

$$\text{Carbon, \%} = \frac{B \times 27.289}{C}$$

where  $A$  = increase in weight of moisture absorption bulb, in grams  
 $B$  = increase in weight of  $\text{CO}_2$  absorption bulb, in grams  
 $C$  = grams of sample used

NOTE 28.—It is recognized that formation of oxides of nitrogen during the combustion procedure may lead to slightly high results for carbon. However, extensive study of this effect by five laboratories led to the conclusion that error so incurred would not be significant in commercial application. In certain research applications, where accuracy of a higher order is required, means of removing oxides of nitrogen prior to water and carbon dioxide absorption should be included.

### NITROGEN

39. The determination of nitrogen shall be made by either the Kjeldahl-Gunning method or the alternate methods described in Sections 40 to 44. In these procedures nitrogen is converted into ammonium salts by destructive digestion of the sample with a hot, catalyzed mixture of concentrated sulfuric acid and potassium sulfate. These salts are subsequently decomposed in a hot alkaline solution from which the ammonia is recovered by distillation, and finally determined by alkalimetric or acidimetric titration.

40. *Apparatus. Digestion Unit.*—An electrical heater of approximately 500-watt minimum rating or a gas burner of comparable capacity; either type of heater shall be provided with adequate means of control to maintain digestion rates as described in Note 29. Commercially made, multiple-unit digestion racks provided with fume exhaust ducts may be used.

NOTE 29.—If commercially made electrical heaters are used, auxiliary voltage control equipment, such as an autotransformer, may be needed to maintain the specified rates of digestion and distillation.

*Distillation Unit.*—An electrical heater or gas burner as described above; either type shall be provided with adequate means of control to maintain distillation rates as described in Note 29. Commercially made, multiple-unit distillation racks provided with water-cooled glass or block tin condensers may be used.

*Condenser.*—A glass condenser, water-cooled, having a minimum jacket length of 500 mm. This apparatus is not ordinarily required when a commercially made distillation rack is used.

Kjeldahl digestion flask, of heat-resistant<sup>20</sup> glass, having a capacity of 500 or 800 ml.

Kjeldahl connecting bulb, cylindrical type, 45 mm. in diameter by 100 mm. long, or larger, with curved inlet and outlet tubes.

Erlenmeyer flask, having a capacity of 250 or 300 ml.

Glass connecting tube, approximately 10 mm. in outside diameter by 200 mm. long.

Rubber tubing, short piece.

41. *Reagents. Alkali Solution.*—Dissolve 80 g. of potassium sulfide ( $\text{K}_2\text{S}$ ) and 330 g. of sodium hydroxide ( $\text{NaOH}$ ) in water and dilute to 1 liter. The use of ap-

<sup>20</sup> Pyrex glass has been found satisfactory for this purpose.

appropriate amounts of sodium sulfide ( $\text{Na}_2\text{S}$ ) or potassium hydroxide ( $\text{KOH}$ ) may be substituted for the above, if desired (Note 30, paragraph (c)).

**Ethyl Alcohol (95%).**—Ethyl alcohol conforming to Formula No. 30 or 2A of the U. S. Bureau of Internal Revenue. Methyl alcohol may be used.

**Mercury, metal** (Note 30).

**Potassium permanganate** ( $\text{KMnO}_4$ ), crystals.

**Potassium sulfate** ( $\text{K}_2\text{SO}_4$ ), crystals.

**Sucrose**, National Bureau of Standards primary-standard grade.

**Sulfuric Acid** (sp. gr. 1.84).—Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ).

**Zinc**, mossy or granular.

**NOTE 30.**—Other satisfactory and permissible catalysts for the digestion, together with the quantities of  $\text{K}_2\text{SO}_4$  required in their use, are as follows:

(a) Five grams of a mixture containing 32 parts by weight of  $\text{K}_2\text{SO}_4$ , 5 parts by weight of mercuric sulfate ( $\text{HgSO}_4$ ), and 1 part by weight of selenium.

(b) Three-tenths gram of mercuric selenite ( $\text{HgSeO}_3$ ) with 7 to 10 g. of  $\text{K}_2\text{SO}_4$ .

(c) Three-tenths gram of cupric selenite dihydrate ( $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ ) with 7 to 10 g. of  $\text{K}_2\text{SO}_4$ . When this mixture is used, the addition of a sulfide to the alkali solution is not necessary.

**Reagents Required Only for Kjeldahl-Gunning Method.** **Methyl Red Indicator Solution** (0.4 to 1 g. per liter).—Dissolve 0.04 to 0.1 g. of methyl red in 50 ml. of 95% ethyl alcohol or methyl alcohol and add 50 ml. of water. Bromocresol green solutions of equal concentrations may be used.

**Sodium Hydroxide, Standard Solution** (0.1 to 0.2 N).—Prepare and accurately standardize a 0.1 to 0.2 N sodium hydroxide ( $\text{NaOH}$ ) solution against a primary standard.

**Sulfuric Acid** (0.2 N).—Prepare and standardize a 0.2 N sulfuric acid ( $\text{H}_2\text{SO}_4$ ) solution. The solution need not be standardized against a primary standard.

**Reagents Required only for Alternate Method.** **Boric Acid Solution** (50 g. per liter).—Dissolve 5 g. of boric acid ( $\text{H}_3\text{BO}_3$ ) in 100 ml. of boiling water. Allow to cool before use.

**Mixed Indicator Solution.**—Prepare a solution containing 0.125% methyl red and 0.083% methylene blue in 95% ethyl alcohol or in methyl alcohol. Prepare a fresh solution at bimonthly intervals.

**Sulfuric Acid** (0.1 to 0.2 N).—Prepare and accurately standardize a 0.1 to 0.2 N sulfuric acid ( $\text{H}_2\text{SO}_4$ ) solution against a primary standard; hydrochloric acid ( $\text{HCl}$ ) of similar concentration may be substituted.

**42. Sample.**—Weigh approximately 1 g. (weighed to the nearest 1. mg.) of air-dry sample ground to pass a No. 60 (250 micron) or finer sieve, into a weighing scoop. In the case of coke and anthracite, grinding the sample to pass a No. 200 (74 micron) or finer sieve is recommended.

**43. Procedure for Kjeldahl-Gunning Method.**—(a) Carefully transfer the sample into a 500- or 800-ml. Kjeldahl flask containing 7 to 10 g. of  $\text{K}_2\text{SO}_4$  and 0.6 to 0.8 g. of mercury (Note 30). Add 30 ml. of  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) to the mixture by pouring it down the neck of the flask with rotation, in order to wash any adherent sample material into the mixture. Swirl the contents of the flask several times to ensure thorough mixing and wetting of the sample. Incline the flask at an angle of  $45^\circ$  to  $60^\circ$  on the digestion heater in a fume hood (Note 31), and heat the contents to boiling, controlling the heat input in such a manner that the  $\text{H}_2\text{SO}_4$  vapors condense no more than halfway up the neck of the flask (Note 29). Continue the

boiling until all sample particles are oxidized, as evidenced by a nearly colorless solution, or for at least 2 hours after the solution has reached a straw-colored stage. The total time of digestion will require 3 to 6 hours, except in the case of coke and anthracite, which may require 12 to 16 hours (Note 32). When the digestion is completed and the solution has cooled, a few crystals of  $\text{KMnO}_4$  may be added to ensure complete oxidation; further heating may be necessary to destroy the excess permanganate and decolorize the solution.

NOTE 31.—When fume exhaust ducts or hoods are not available a Hengar tube may be inserted in the neck of the flask.

NOTE 32.—Addition of 0.1 g. of chromic anhydride ( $\text{CrO}_3$ ) to the digestion mixture has been found very helpful in reducing the time of digestion for coke.

(b) Dilute the cooled digestion mixture to about 300 ml. with cold water, and remove any heat of dilution by cooling with water. Meanwhile, measure into the 250- or 300-ml. Erlenmeyer flask, 20.0 ml. of 0.2  $N$   $\text{H}_2\text{SO}_4$  and add six drops of methyl red or bromcresol green indicator solution. Attach the glass connecting tube to the discharge end of the condenser, using a short piece of rubber tubing as a seal. Incline the Erlenmeyer flask at a suitable angle, and insert this tube so that the end is immersed to the maximum depth in the acid. Add 1 to 2 g. of granular zinc to the mixture in the Kjeldahl flask (two or three small pieces if mossy zinc is used), and slowly add 100 ml. of the alkali solution so that it forms a distinct layer under the acid solution. This may be accomplished by inclining the flask at an angle of  $45^\circ$  to  $60^\circ$  and pouring the alkali solution down the neck. Failure to maintain discrete layers during this operation may lead to loss of ammonia. Quickly connect the flask to the distilling condenser through the Kjeldahl connecting bulb, and then swirl the contents to promote thorough mixing.

(c) Bring the contents of the Kjeldahl flask to a boil carefully, in order to avoid violent bumping, and then distill the ammonia over into the acid solution in the Erlenmeyer flask. Continue the distillation at a maximum rate of approximately 350 ml. per hour until 150 to 175 ml. of distillate have been collected. Discontinue the boiling, and remove the glass connecting tube from the condenser and Erlenmeyer flask. Rinse the tube with distilled water, collecting the washings in the Erlenmeyer flask, and then back-titrate the excess acid with 0.1 to 0.2  $N$   $\text{NaOH}$ .

(d) Run a blank determination in the same manner as described above, using approximately 1 g. of sucrose (weighed to the nearest milligram) as the sample material (Note 33).

NOTE 33.—Blank determinations must be made to correct for nitrogen from sources other than the sample. A blank determination shall be made whenever a new batch of any one reagent is used in the analysis.

(e) Calculation.—Calculate the percentage of nitrogen in the sample as follows:

$$\text{Nitrogen, \%} = \frac{(B - A)N \times 0.014}{C} \times 100$$

where  $A$  = milliliters of 0.1 to 0.2  $N$   $\text{NaOH}$  solution required for titration of the sample  
 $B$  = milliliters of 0.1 to 0.2  $N$   $\text{NaOH}$  solution required for titration of the blank  
 $N$  = normality of the  $\text{NaOH}$  solution  
 $C$  = grams of sample used

**44. Procedure for Alternate Method.**—Digest the sample as described in Section 43(a).

Dilute and cool the digestion mixture as described in Section 43(b). Add to the 250- or 300-ml. Erlenmeyer flask approximately 20 ml. of  $\text{H}_3\text{BO}_3$  solution and six drops of mixed indicator solution. Then proceed as described in the remainder of Section 43(b).

Distill the ammonia into the  $\text{H}_3\text{BO}_3$  solution exactly as described in Section 43(c), and finally titrate the ammonia with 0.2  $N$   $\text{H}_2\text{SO}_4$ .

Run a blank determination in the same manner as described above, using approximately 1 g. (weighed to the nearest milligram) of sucrose as the sample material (Note 33).

**Calculation.**—Calculate the percentage of nitrogen in the sample as follows:

$$\text{Nitrogen, \%} = \frac{(A - B)N \times 0.014}{C} \times 100$$

where  $A$  = milliliters of 0.2  $N$   $\text{H}_2\text{SO}_4$  required for titration of the sample

$B$  = milliliters of 0.2  $N$   $\text{H}_2\text{SO}_4$  required for titration of the blank

$N$  = normality of the  $\text{H}_2\text{SO}_4$

$C$  = grams of sample used

### OXYGEN

**45. Calculation.**—There being no satisfactory direct ASTM method of determining oxygen, it shall be calculated by subtracting from 100 the sum of the percentages of hydrogen, carbon, nitrogen, sulfur, moisture, and ash. The result so obtained is affected by the errors incurred in the other determinations and also by the changes in weight of the ash-forming constituents on ignition.

### CALCULATION OF ANALYSES TO DRY BASIS

**46. Calculations. Coal Appearing Dry.**—Calculate the analysis of the coal passing the No. 60 sieve, which has become partly air-dried during sampling, to the dry-coal basis by dividing each result by 1 minus its content of moisture, as determined in accordance with Section 4. Compute the analysis of the coal "as received" from the dry-coal analysis by multiplying by 1 minus the total moisture found in the sample passing a No. 20 sieve.

**Coal Appearing Wet.**—Correct the moisture found in the air-dried sample (see Section 5) passing a No. 20 sieve to total moisture "as received," as follows:

$$TM = \left( M \times \frac{100 - L}{100} \right) + L$$

where  $TM$  = total moisture of coal "as received"

$L$  = percentage of air-drying loss

$M$  = percentage of moisture in air-dried sample passing a No. 20 sieve

Calculate the analysis to "dry-coal" and "as-received" bases as described in Section 3 for dry coal, using for the "as-received" calculation the total moisture as calculated by the above formula in place of the moisture found in the coal passing a No. 20 sieve (Note 31).

NOTE 34.—The accuracy of the method of preparing laboratory samples should be checked frequently by resampling the rejected portions and preparing a duplicate sample. The ash in the two samples should not differ by more than the following:

No carbonates present.....	0.4%
Considerable carbonate and pyrite present.....	0.7%
Coals with more than 12 per cent ash, containing considerable carbonate and pyrite.....	1.0%

**Coal Appearing Wet or Dry, Sampled by Ball-Mill Method.**—As all the analytical determinations are made on the air-dried sample passing a No. 60 sieve, calculate the analysis to “as-received” and “dry-coal” bases from the analysis of the air-dried coal as follows:

*Calculation from Analysis of “Air-Dried” Coal to Coal “As Received,” All Figures Expressed in per cent:*

$$\text{Moisture “as received”} = \text{moisture} \times \frac{100 - L}{100} + L$$

$$\text{Volatile matter “as received”} = \text{volatile matter} \times \frac{100 - L}{100}$$

$$\text{Fixed carbon “as received”} = \text{fixed carbon} \times \frac{100 - L}{100}$$

$$\text{Ash “as received”} = \text{ash} \times \frac{100 - L}{100}$$

$$\text{Sulfur “as received”} = \text{sulfur} \times \frac{100 - L}{100}$$

$$\text{Hydrogen “as received”} = \text{hydrogen} \times \frac{100 - L}{100} + \frac{L}{9}$$

$$\text{Carbon “as received”} = \text{carbon} \times \frac{100 - L}{100}$$

$$\text{Nitrogen “as received”} = \text{nitrogen} \times \frac{100 - L}{100}$$

$$\text{Oxygen “as received”} = \text{oxygen} \times \frac{100 - L}{100} + \frac{8L}{9}$$

$$\text{Calories “as received”} = \text{calories} \times \frac{100 - L}{100}$$

where  $L$  = air-drying loss.

*Calculation from Analysis of “Air-Dried” Coal to “Dry” Coal, All Figures Expressed in per cent:*

$$\text{Volatile matter in “dry coal”} = \text{volatile matter} \times \frac{100}{100 - \text{moisture}}$$

$$\text{Fixed carbon in "dry coal"} = \text{fixed carbon} \times \frac{100}{100 - \text{moisture}}$$

$$\text{Ash in "dry coal"} = \text{ash} \times \frac{100}{100 - \text{moisture}}$$

$$\text{Sulfur in "dry coal"} = \text{sulfur} \times \frac{100}{100 - \text{moisture}}$$

$$\text{Hydrogen in "dry coal"} = (\text{hydrogen} - \frac{1}{8} \text{ moisture}) \times \frac{100}{100 - \text{moisture}}$$

$$\text{Carbon in "dry coal"} = \text{carbon} \times \frac{100}{100 - \text{moisture}}$$

$$\text{Nitrogen in "dry coal"} = \text{nitrogen} \times \frac{100}{100 - \text{moisture}}$$

$$\text{Oxygen in "dry coal"} = (\text{oxygen} - \frac{8}{9} \text{ moisture}) \times \frac{100}{100 - \text{moisture}}$$

$$\text{Calories in "dry coal"} = \text{calories} \times \frac{100}{100 - \text{moisture}}$$

### REPRODUCIBILITY OF RESULTS

**47. Reproducibility of Results.**—The permissible differences between two or more determinations shall not exceed the values given in Table 31-3.

### DETERIORATION OF COAL SAMPLES

**48.** Since coal samples on standing oxidize and change in composition, it is essential that they be analyzed as soon as possible after collecting the gross samples. If the Btu determination is an important consideration in the sale of coal, the time elapsed between sampling and analysis shall not exceed 30 days.

### FUSIBILITY OF COAL ASH<sup>21</sup>

This method covers the observation of the temperatures at which triangular pyramids (cones) prepared from coal ash attain and pass through certain defined stages of fusing and flow when heated at a specified rate in controlled, mildly reducing, and where desired, oxidizing atmospheres.

The method is empirical, and strict observance of the requirements and conditions is necessary to obtain reproducible temperatures and enable different laboratories to obtain concordant results.

**Definitions and Symbols.**—The critical temperature points to be observed shall be as follows, denoting the atmosphere used:

(a) **Initial Deformation Temperature, A.**—The temperature at which the first rounding of the apex or the edges of the cone occurs. Shrinkage or warping of the cone shall be ignored if the tip and edges remain sharp. In Fig. 31-9, cone 1

<sup>21</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Proposed as ASTM D1857-61T.

TABLE 31-3. PERMISSIBLE DIFFERENCES IN RESULTS

	Permissible Differences	
	Same Laboratory	Different Laboratories
ON LABORATORY SAMPLES, CRUSHED TO PASS A No. 20 (840 MICRON) SIEVE		
Moisture:		
Under 5 per cent.....	0.2	0.3
Over 5 per cent.....	0.3	0.5
ON LABORATORY SAMPLES, CRUSHED TO PASS A No. 60 (250 MICRON) SIEVE		
Moisture:		
Under 5%.....	0.2	0.3
Over 5%.....	0.3	0.5
Ash:		
No carbonates present.....	0.2	0.3
Carbonates present.....	0.3	0.5
Coals with more than 12% of ash, containing carbonate and pyrite.....	0.5	1.0
Volatile Matter:		
High-temperature Coke.....	0.2	0.4
Anthracite.....	0.3	0.6
Semianthracite, bituminous coal, low-temperature coke, and chars.....	0.5	1.0
Subbituminous coal.....	0.7	1.4
Lignite and peat.....	1.0	2.0
Sulfur:		
Coal, under 2%.....	0.05	0.10
Coal, over 2%.....	0.10	0.20
Coke.....	0.03	0.05
Ultimate Analysis:		
Carbon.....	0.3	...
Hydrogen.....	0.07	...
Nitrogen.....	0.05	...

shows an unheated cone; cone 2 shows a typical appearance of a cone at the initial deformation stage.

(b) **Softening Temperature, Spherical, B.**—The temperature at which the cone has fused down to a spherical lump in which the height is equal to the width at the base as shown in Fig. 31-9, cone 3.

(c) **Softening Temperature, Hemispherical, C.**—The temperature at which the cone has fused down to a hemispherical lump at which point the height is one-half the width of the base as shown in Fig. 31-9, cone 4.

(d) **Fluid Temperature, D.**—The temperature at which the fused mass has spread out in a nearly flat layer with a maximum height of  $\frac{1}{16}$  in. as shown in Fig. 31-9, cone 5.

**Apparatus and Materials. Furnace.**—Any gas-fired or electric furnace conforming to the following requirements may be used:

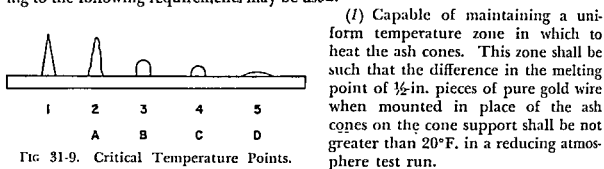


FIG 31-9. Critical Temperature Points.

(1) Capable of maintaining a uniform temperature zone in which to heat the ash cones. This zone shall be such that the difference in the melting point of  $\frac{1}{2}$ -in. pieces of pure gold wire when mounted in place of the ash cones on the cone support shall be not greater than  $20^{\circ}\text{F.}$  in a reducing atmosphere test run.

(2) Capable of maintaining the desired atmosphere surrounding the cones during heating. The composition of the atmosphere, reducing or oxidizing, shall be maintained within the limits specified in the next section. The desired atmosphere in the gas-fired furnace surrounding the cones shall be obtained by regulation of the ratio of gas to air in the combustion mixture. The desired atmosphere in the electric furnace shall be obtained by means of gases introduced into the heating chamber. The muffle shall be gas impervious, free from cracks, and the closure-plug tight fitting. The gas supply tube shall be sealed to the back wall of the preheating chamber, and shall not extend to the front of the preheating chamber against the perforated baffle.

(3) Capable of regulation so that the rate of temperature rise shall be  $15^{\circ} \pm 5^{\circ}\text{F.}$  per minute.

(4) Providing means of observing the ash cones during the heating. Observation on the same horizontal plane as the cone-support surface shall be possible.

**Cone Mold.**—A commercially available cone mold as shown in Fig. 31-10. The cone shall be  $\frac{3}{4}$  in. in height and  $\frac{1}{4}$  in. in width at each side of the base which is an equilateral triangle. A steel spatula with a pointed tip, ground off to fit the cone depression in the mold, is suitable for removal of the ash cone.

**Optical pyrometer or thermocouple,** for temperature measurements, conforming to the following requirements:

(1) **Optical Pyrometer.**—An optical pyrometer of the disappearing filament type shall be used. The instrument shall have been calibrated to be accurate within  $20^{\circ}\text{F.}$  up to  $2550^{\circ}\text{F.}$  and within  $30^{\circ}\text{F.}$  from  $2550^{\circ}$  to  $2900^{\circ}\text{F.}$  (Note 1). The pyrometer filament shall be sighted on the cones until the softening point temperature C (Fig. 31-9) has been passed, and then sighted on the cone support. The pyrometer shall have readable graduations not larger than  $10^{\circ}\text{F.}$



NOTE 1.—The pyrometer equipment shall be standardized periodically by a suitably equipped standardizing laboratory such as that of the National Bureau of Standards, or checked periodically against equipment certified by the Bureau of Standards.

(2) *Thermocouple*.—A thermocouple (Note 2) of platinum and platinum-rhodium, protected from the furnace gases by a glazed porcelain sheath, shall be used with a high-resistance millivoltmeter or potentiometer that has been calibrated to be accurate and readable to within 10°F. The sheath shall be sealed to the furnace wall by alundum cement. The hot junction of the thermocouple shall touch the

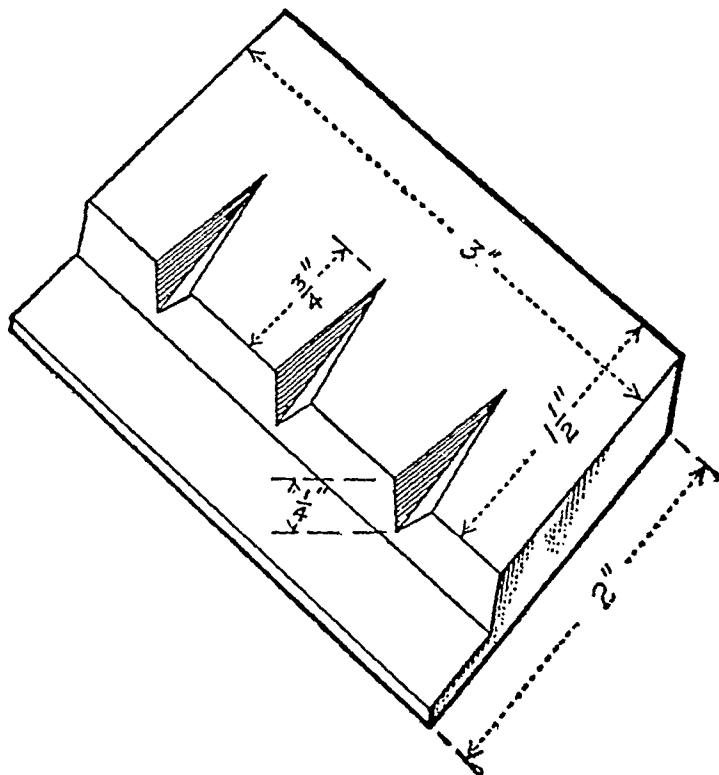


FIG. 31-10. Brass Cone Mold.

end of the sheath and shall be located in the center of the muffle and immediately to the rear of the cones. The potentiometer or millivoltmeter shall be so located or adequately shielded as to prevent radiant and convection heating of the cold junction. The room temperature compensator shall be adjusted to the existing temperature.

NOTE 2.—The thermocouple shall be checked periodically against a certified thermocouple. The thermocouple protective sheath shall be checked periodically for cracks.

*Ash-Cone Refractory Support*.—The ash cones shall be mounted on a refractory base composed of a mixture of equal parts by weight of kaolin and alumina conforming to the following requirements:

- (1) *Kaolin*.—NF-Grade powder passing a 74-micron (No. 200) sieve.
- (2) *Aluminum Oxide*.—Reagent grade ignited powder passing a 149-micron (No. 100) sieve.

*Refractory Support Mold*.—A mold with flat top and bottom surfaces to provide a refractory support of suitable thickness to minimize warping. A side-mold not

over  $\frac{1}{4}$  in. high of any convenient shape, placed on an iron plate so that the top surface of the refractory mix can be struck off flat and parallel to the base by means of a straightedge is satisfactory. For electric furnace use, legs not over  $\frac{1}{8}$  in. long may be provided on the corners of the cone support by suitable holes bored in the iron base plate of the mold.

**Gold and Nickel Wire.**—Pure gold and pure nickel wires, having melting points in a reducing atmosphere of 1945°F. and 2646°F., respectively, shall be used in the gas-fired furnace. Gold wire shall be used in the electric furnace.

**Test Atmosphere. Gas-Fired Furnace. (1) Reducing Atmosphere Test.**—A mildly reducing atmosphere surrounding the cones shall be maintained during the test in the gas-fired furnace. Hydrogen, hydrocarbons, and carbon monoxide shall be considered as reducing gases; oxygen, carbon dioxide, and water vapor shall be considered as oxidizing gases. Nitrogen is inert. The ratio by volume of reducing gases in the atmosphere shall be between the limits of 20 to 80 and 80 to 20,<sup>22</sup> that is, on a nitrogen-free basis, the total amount of reducing gases present shall be between the limits of 20 and 80% by volume. A flame 6 to 8 in. in height and tinged with yellow above the furnace outlet has been found to provide an atmosphere within the specified limits.

**(2) Oxidizing Atmosphere Test.**—An atmosphere containing a minimum amount of reducing gases shall be maintained surrounding the cones during the test in the gas-fired furnace. On a nitrogen-free basis, the volume of reducing gases present in the atmosphere shall not exceed 10% by volume. Combustion with the maximum possible quantity of air with preservation of the specified rate of temperature increase has been found to provide an atmosphere within the specified limits. A completely blue flame, not over 2 in. in height above the outlet at the beginning of the test, provides the desired atmosphere; and, by regulation of the combustion gas-air ratio, the specified atmosphere and temperature rise can be maintained.

**Electric Furnace. (1) Reducing Atmosphere Test.**—A regulated flow of gas of the nominal composition, 60% carbon monoxide and  $40 \pm 5\%$  carbon dioxide by volume<sup>23</sup> shall be maintained in the heating chamber throughout the test (Note 3) in the electric furnace. The gas stream shall be regulated by any convenient means to provide a measured flow of 1.3 to 1.5 furnace volumes per minute.

**(2) Oxidizing Atmosphere Test.**—A regulated stream of air shall be maintained throughout the test in the electric furnace. The gas stream shall be regulated by any convenient means to provide a measured flow of 1.3 to 1.5 furnace volumes per minute.

**NOTE 3.**—New cylinders of the mixed gas for which a certified analysis is not available should be mixed before use by supporting the cylinder at an angle with the bottom in a pan of warm water while circulating cold water across the upper part of the cylinder for several hours. Certified analyses of each cylinder or batch can be obtained for a small extra charge.

**Preparation of Ash.**—Use coal or coke passing a 250-micron (No. 60) sieve prepared in accordance with the Methods of Laboratory Sampling and Analysis of Coal and Coke (ASTM D271, p. 1145) to obtain the ash by incineration in a well-ventilated muffle furnace. The quantity of coal or coke required will vary with

<sup>22</sup> For information concerning the effect of various atmospheres, see U. S. Bureau of Mines Bulletin 129 (1918).

<sup>23</sup> This gas is available from the Matheson Gas Co., Inc.

the ash content; usually 3 to 5 g. of ash will be sufficient for cones for several check determinations, if necessary. Spread out the coal or coke in a layer not over  $\frac{1}{4}$  in. in depth in a fireclay or porcelain roasting dish. Place the dish in the cold muffle or on the hearth at a low temperature and gradually heat to redness at such a rate as to avoid mechanical loss from too rapid expulsion of volatile matter (Note 4). Complete the conversion to ash at a temperature of 1470° to 1650°F. Transfer the ash to an agate mortar (Note 5) and grind it so that it will pass a 74-micron (No. 200) sieve. Then spread the ash in a thin layer in a fireclay, silica, or porcelain dish and ignite it in a stream of oxygen for 1½ hours at 1470° to 1560°F. to ensure complete and uniform oxidation of the ash. Any tube or muffle-type furnace which, when supplied with an oxygen flow of not less than one furnace volume in 5 minutes, will maintain a highly oxidizing atmosphere and will be suitable.

NOTE 4.—A heating rate conforming to that used for the modified ash determination specified in Section 14, Note 7(a) of Method D271 is satisfactory.

NOTE 5.—A mechanical agate mortar grinder will save time where many determinations are made. An iron mortar or pestle must not be used.

*Preparation of Cones.*—Thoroughly mix the ignited ash in a mechanical mixer or on a sheet of glazed paper or oilcloth by raising first one corner to roll the ash over, and then raising each of the other corners in rotation in the same manner until each corner has been raised five times or more.

Take sufficient ash for the number of cones desired from various parts of the bulk ash. Moisten the ash with a few drops of a clear, filtered (if necessary) 10% solution of dextrin containing 0.1% salicylic acid as a preservative and work it into a stiff plastic mass with a spatula. Press the plastic material firmly with a spatula into the cone mold to form the triangular pyramids. Strike off the exposed surfaces of the material smooth and remove the cones from the mold by applying pressure at the base with a suitably pointed spatula. Previous coating of the mold with a thin layer of petroleum jelly, thinned with kerosene (if necessary), aids in preventing adherence of the cones to the mold and in providing the sharp point and edges desired in the cone. With certain coal ashes, cones with sharp points and edges can be obtained using distilled water in place of the dextrin solution and without the use of petroleum jelly.

Place the cones in a suitable location to dry sufficiently to permit handling without deformation. Mount the dried cone vertically on a freshly prepared refractory base. Moisten a portion of the well-mixed kaolin-alumina mixture with the minimum amount of water to make a workable, but stiff, plastic mass, and firmly press it into the support mold. Strike off the surface of the mass flat and smooth with a steel spatula, moistening with one or two drops of water if necessary to obtain a smooth surface. A number of cones may be mounted on one base. Make shallow, triangular depressions, not over  $\frac{1}{32}$  in. in depth, with a triangular file ground to the correct size to produce a depression to fit the base of the cone, and locate the cones sufficiently distant from adjacent cones so that no merging of the fusing material of the cones shall occur during the test. Mount the cones vertically in the depressions while the base is still wet without the use of ash or refractory as a mounting aid (Note 6).

NOTE 6.—The intent of the triangular depression is to enable the cones to be mounted in a sufficiently stable manner to permit handling of the prepared support with cones.

Mount  $\frac{1}{2}$ -in. lengths of gold and nickel wire vertically on each support by inserting wire into the support before drying. For the reducing atmosphere test in the electric furnace, do not use nickel wire.

Dry the mounted cones in a drying oven at 220°F. for 1½ hours, remove the support mold, and ignite the mounted cones in an open muffle at 1100°F. for 30 minutes to remove all carbonaceous material (Note 7).

NOTE 7.—If no organic material has been used in the preparation of the mounted cones, this ignition step may be omitted. The drying step must be retained.

**Procedure. Reducing Atmosphere Test.**—(1) Place the mounted test cones in the furnace at a temperature of not over 1470°F. for the gas-fired furnace, and not over 750°F. for the electric furnace in order to provide sufficient time to purge the air from the uniform temperature zone and establish the desired atmosphere.

(2) If the furnace temperature is below the respective temperature specified in Item (1), raise it rapidly to the specified temperature; then control the rate of heating to give a rate of temperature increase of  $15^{\circ} \pm 5^{\circ}\text{F.}$  per minute. Maintain this rate throughout the test.

(3) Establish the mildly reducing atmosphere surrounding the cones, as specified in the section on Test Atmosphere (p. 1174), at the temperature specified in Item (1) for the respective furnace type. Maintain this atmosphere throughout the test (Note 8).

NOTE 8.—At temperatures of the order of 2500° to 2600°F. and above in the gas-fired furnace, it may not be possible to maintain the reducing gases above the 20% by volume limit specified while also preserving the specified rate of temperature increase. At such temperatures, the effect of the atmosphere is not so critical as the maintenance of the specified heating rate. Every effort shall be made to maintain the reducing gases as near the 20% by volume level as possible at such temperatures.

**Oxidizing Atmosphere Test.**—(1) Place the mounted test cones in the furnace at a temperature of not over 1470°F. for the gas-fired furnace, and not over 750°F. for the electric furnace. If the furnace temperature is below the respective temperature specified in Item (1), raise it rapidly to the specified temperature, then control the rate of heating to give a rate of temperature increase of  $15^{\circ} \pm 5^{\circ}\text{F.}$  per minute. Maintain this rate throughout the test.

(2) Establish the oxidizing atmosphere surrounding the cones, as specified in the section on Test Atmosphere (p. 1174), at the temperature specified in Item (1) for the respective furnace type. Maintain this atmosphere throughout the test.

Under the condition of the test, the pure gold and pure nickel wires seldom melt at the exact temperatures (see Gold and Nickel Wire, p. 1174). The test results shall be rejected if the melting temperatures do not fall within the following ranges:

*Reducing atmosphere test:*

Gold wire, °F. ....	1930-1950
Nickel wire, °F. ....	2630-2650

*Oxidizing atmosphere test:*

Gold wire, °F. ....	1930-1950
Nickel wire, °F. ....	Should not melt

**Precision.—Repeatability (Single Operator and Apparatus).** For each point, the difference for the critical point temperature between two separate furnace runs shall not exceed  $\pm 50^{\circ}\text{F.}$

*Reproducibility (Different Operators and Apparatus).*—For each point, the difference for the critical point temperature between two furnace runs shall not exceed the following:

°F.

*For reducing atmosphere:*

Initial deformation point, <i>A</i> . . . . .	125
Softening point, spherical, <i>B</i> . . . . .	100
Softening point, hemispherical, <i>C</i> . . . . .	100
Fluid point, <i>D</i> . . . . .	150

*For oxidizing atmosphere:*

Initial deformation point, <i>A</i> . . . . .	100
Softening point, spherical, <i>B</i> . . . . .	100
Softening point, hemispherical, <i>C</i> . . . . .	100
Fluid point, <i>D</i> . . . . .	100

## METHOD OF TEST FOR GROSS CALORIFIC VALUE OF SOLID FUEL BY THE ADIABATIC BOMB CALORIMETER <sup>24</sup>

1. This method describes the procedure for determining the gross calorific value of solid fuel by the adiabatic bomb calorimeter.

2. Calorific value is determined in this method by burning a weighed sample in an adiabatic oxygen bomb calorimeter under controlled conditions. The calorific value is computed from temperature observations made before and after combustion, taking proper allowance for thermometer and thermochemical corrections.

3. *Definitions and Units.*—Calorific value is the heat of combustion of a substance. It is usually expressed in British thermal units per pound. (Calorific value may also be computed in calories per gram or joules per gram when required.)

One Btu (British thermal unit) equals 1055.07 absolute joules.

One international steam table calorie equals 4.1868 absolute joules.

Gross calorific value is the heat produced by combustion of a unit quantity of solid fuel, at constant volume, in an oxygen bomb calorimeter under specified conditions such that all water in the products remains in liquid form. (Refer to ASTM D407-44, p. 1276.)

Net calorific value is a lower value calculated from the gross calorific value. It is equivalent to the heat produced by combustion of a unit quantity of solid fuel at constant atmospheric pressure, under conditions such that all water in the products remains in the form of vapor. (Refer to ASTM D407-44, p. 1277.)

Water equivalent, heat capacity, or energy equivalent is the energy required to raise the temperature of the calorimeter one degree, expressed as Btu per pound per degree Centigrade or degree Fahrenheit per gram of sample. (This is the number that is multiplied by the temperature rise and divided by the sample weight in grams, to give the heating value.)

Temperature is measured in either degrees Centigrade or degrees Fahrenheit. Temperatures may also be recorded in ohms or other units when using electric thermometers. Consistent units must be used in both the standardization and actual calorific determination.

Time is expressed in minutes.

Weights are measured in grams.

<sup>24</sup> Fifth Draft, completed and approved by the Task Group C (Chairman A. O. Blatter, Chief Chemist, Union Electric Co., St. Louis, Missouri), of the ASTM Committee D-5.

**4. Apparatus. Test Room.**—The apparatus should be operated in a room or area free from drafts which can be kept at a reasonably uniform temperature for the time required for the determination. The apparatus should be shielded from direct sunlight and radiation from other sources.

**Oxygen Bomb.**—The oxygen bomb shall be constructed of materials which are not affected by the combustion process or products sufficiently to introduce measurable heat input or alteration of end products. If the bomb is lined with platinum or gold, all openings shall be sealed to prevent combustion products from reaching the base metal. The bomb must be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There must be no gas leakage during a test. The bomb must be capable of withstanding a hydrostatic pressure test to 3000 psig at room temperature without stressing any part beyond its elastic limit.

**Calorimeter.**—The calorimeter (Note 1) vessel shall be made of metal (preferably copper or brass) with a tarnish-resistant coating, and with all outer surfaces highly polished. Its size shall be such that the bomb will be completely immersed in water when the calorimeter is assembled. It shall have a device for stirring the water thoroughly and at a uniform rate, but with minimum heat input. Continuous stirring for 10 minutes shall not raise the calorimeter temperature more than 0.01°C. (0.02°F.) starting with identical temperatures in the calorimeter, room, and jacket. The immersed portion of the stirrer shall be coupled to the outside through a material of low heat conductivity.

**NOTE 1.**—As used in this method, the term "calorimeter" describes the bomb, the vessel with stirrer, and the water in which the bomb is immersed.

**Jacket.**—The calorimeter shall be completely enclosed within a stirred water jacket and supported so that its sides, top, and bottom are approximately 1 cm. from the jacket walls. The jacket shall have provisions for rapidly adjusting the jacket temperature to equal that of the calorimeter for adiabatic operation. It must be constructed so that any water evaporating from the jacket will not condense on the calorimeter.

**Thermometers.**—Temperatures in the calorimeter and jacket shall be measured with the following thermometers or combinations thereof:

1. *Etched stem, mercury-in-glass thermometers* such as No. 56 F or 56 C, meeting ASTM Specifications E1,<sup>25</sup> may be used. Other thermometers of equal or better accuracy are satisfactory. These thermometers shall be tested for accuracy against a known standard (preferably by the National Bureau of Standards) at intervals no larger than 2.5°F. or 2.0°C. over the entire graduated scale. The maximum difference in correction between any two test points shall not be more than 0.02°C. or 0.05°F.

2. *Beckmann differential thermometer*, having a range of approximately 6°C. in 0.01°C. subdivisions reading upward. Each of these thermometers shall be tested for accuracy against a known standard (preferably by the National Bureau of Standards) at intervals no larger than 1°C. over the entire graduated scale. The maximum difference between any two test points shall not be more than 0.02°C.

3. *Calorimetric type platinum resistance thermometer*, 25 ohm, tested for accuracy against a known standard (preferably by the National Bureau of Standards).

<sup>25</sup> 1961 Book of ASTM Standards, Part 8, p. 1741.

**Thermometer Accessories.**—A magnifier is required for reading mercury-in-glass thermometers to one-tenth of the smallest scale division. This shall have a lens and holder designed so as to introduce no significant errors due to parallax. A Wheatstone bridge and galvanometer capable of measuring resistance to 0.0001 ohm are necessary for use with resistance thermometers.

**Sample Holder.**—Samples shall be burned in an open crucible of platinum, quartz, or acceptable base metal alloy. Base metal alloy crucibles are acceptable if, after a few preliminary firings, the weight does not change significantly between tests.

**Firing Wire.**—The firing wire shall be 10 cm. of No. 34 B & S nickel-chromium alloy wire or 10 cm. of No. 34 B & S iron wire. Platinum wire No. 38 B & S gauge may be used provided constant ignition energy is supplied. Alternately, a cotton thread may be used for ignition in conjunction with the firing wire. In this case, the firing wire shall be just long enough to stretch tautly between the ignition terminals. The lengths of the firing wire and cotton thread shall remain constant for all calibrations.

**Firing Circuit.**—A 6- to 16-volt alternating or direct current is required for ignition purposes with an ammeter or pilot light in the circuit to indicate when current is flowing. A step-down transformer connected to an alternating current lighting circuit or batteries may be used.

**Caution.**—The ignition circuit switch shall be of the momentary double contact type, normally open, except when held closed by the operator. The switch should be depressed only long enough to fire the bomb.

**5. Reagents. Alkali, Standard Solution.**—One milliliter of this solution should be equivalent to 10.0 Btu in the nitric acid titration. Dissolve 20.90 g. of reagent grade anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in distilled water and dilute to 1 liter. The sodium carbonate should be previously dried for 24 hours at 105°C. The buret used for the nitric acid titration must be of such accuracy that estimations to 0.1 ml. can be made.

**Benzoic Acid, Standard.**—Use National Bureau of Standards Benzoic Acid. The crystals shall be pelletized before use. Commercially prepared pellets may be used provided they are made from National Bureau of Standards Benzoic Acid. The value of heat of combustion of benzoic acid, for use in the calibration calculations, shall be in accordance with the value listed in the National Bureau of Standards certificate issued with the standard.

**Methyl Orange, Methyl Red, or Methyl Purple Indicator.**—These indicators may be used, and the selected shall be used consistently in both calibrations and calorific determination.

**Oxygen.**—Oxygen must be free from combustible matter. Oxygen manufactured from liquid air, guaranteed to be greater than 99.5% pure, will meet this requirement. Oxygen made by the electrolytic process may contain a small amount of hydrogen rendering it unfit without purification.

**6. Standardization.**—Determine the water equivalent of the calorimeter as the average of a series of 10 individual runs, made over a period of not less than 3 days nor more than 5 days. To be acceptable, the standard deviation of the series shall be 6.5 Btu per °C. (3.6 Btu per °F.) or less. (Refer to Appendix I on p. 1184 for an illustration showing the necessary calculations.) For this purpose, any individual run may be discarded only if there is evidence indicating incomplete

combustion. If this limit is not met, the entire series shall be repeated until a series is obtained with a standard deviation below the acceptable limit.

The weights of the pellets of benzoic acid in each series should be regulated to yield the same temperature rise as that obtained with the various coal samples tested in the individual laboratories. The usual range of weight is 0.9 to 1.3 g. Make each determination according to the procedure described subsequently in Section 8, and compute the corrected temperature rise,  $t$ , as described in Section 9(a). Determine the corrections for nitric acid and firing wire as described in Section 9(b) and substitute into the following equation:

$$W = \frac{(H)(g) + e_1 + e_3 + e_4}{t}$$

where  $W$  = water equivalent

$H$  = heat of combustion of benzoic acid, as stated in the NBS certificate, Btu per pound

$g$  = weight of benzoic acid, grams

$t$  = corrected temperature rise (Section 9(a))

$e_1$  = titration correction, Btu (Section 9(b))

$e_3$  = fuse wire correction, Btu (Section 9(b))

$e_4$  = cotton thread correction, Btu (if used) (Section 9(b)).

**7. Restandardization.**—Checks on the standard water equivalent shall be made after changing any part of the calorimeter and at least once a month. The test procedure for checking the standard water equivalent factor shall be in accordance with Section 6, except that the required number of individual runs shall be determined in accordance with the following instructions:

1. If a single new standard value exceeds the old standard by  $\pm 6$  Btu per  $^{\circ}\text{C}$ . ( $\pm 4$  Btu per  $^{\circ}\text{F}$ .), the old standard is suspect, thereby requiring a second test.

2. The difference between the two new standards must not exceed 8 Btu per  $^{\circ}\text{C}$ . (5 Btu per  $^{\circ}\text{F}$ .), and the average of the two new standards must not differ from the old standard by more than  $\pm 4$  Btu per  $^{\circ}\text{C}$ . ( $\pm 3$  Btu per  $^{\circ}\text{F}$ .). If these requirements are met, do not change the standard on the calorimeter.

3. If these requirements are not met, two more standards must be run. The range of the four new standards must not exceed 14 Btu per  $^{\circ}\text{C}$ . (8 Btu per  $^{\circ}\text{F}$ .), and the average of the four new standards must not differ from the old standard by more than  $\pm 3$  Btu per  $^{\circ}\text{C}$ . ( $\pm 2$  Btu per  $^{\circ}\text{F}$ .). If these requirements are met, do not change the standard on the calorimeter.

4. If these requirements are not met, a fifth and sixth standard must be run. The range of the six new standards must not exceed 17 Btu per  $^{\circ}\text{C}$ . (10 Btu per  $^{\circ}\text{F}$ .), and the average of the six new standards must not differ from the old standard by more than  $\pm 2$  Btu per  $^{\circ}\text{C}$ . ( $\pm 2$  Btu per  $^{\circ}\text{F}$ .). If these requirements are met, do not change the standard on the calorimeter.

5. If these requirements are not met, four more standards must be run to complete a series of ten runs. The range of these ten results must not exceed 20 Btu per  $^{\circ}\text{C}$ . (12 Btu per  $^{\circ}\text{F}$ .), and the average of the ten new standards must not differ from the old standard by more than  $\pm 1$  Btu per  $^{\circ}\text{C}$ . ( $\pm 1$  Btu per  $^{\circ}\text{F}$ .). If these requirements are met, do not change the standard on the calorimeter.

6. If these requirements are not met, the average value from the ten new standards must be used for the new standard water equivalent, provided that the standard deviation of the series does not exceed 6.5 Btu per  $^{\circ}\text{C}$ . (3.6 Btu per  $^{\circ}\text{F}$ .).



Table 31-4 summarizes the numerical requirements at each stage of restandardization:

TABLE 31-4. TEST VALUES EXCEEDING TABLE LIMITS REQUIRE ADDITIONAL RUNS <sup>a</sup>

No. of Runs	Maximum Range of Results		Maximum Difference between $\bar{X}_1$ and $\bar{X}_2$ <sup>b</sup>	
	Btu/°C.	Btu/°F.	Btu/°C.	Btu/°F.
1	—	—	±6	±4
2	8	5	±4	±3
4	14	8	±3	±2
6	17	10	±2	±2
10	20	12	±1	±1

<sup>a</sup> Values in this table have been rounded off after statistical calculation, and are therefore not precisely in a ratio of 1.8 to 1.0.

<sup>b</sup>  $\bar{X}_1$  = average of original standard.

$\bar{X}_2$  = average of check runs.

**8. Procedure. Weight of Sample.**—Thoroughly mix the analysis sample of coal or coke in the sample bottle and carefully weigh approximately 1 g. of it into the crucible in which it is to be burned. The sample shall be weighed to the nearest 0.1 mg. (Note 2) (Note 3) (Note 4).

NOTE 2.—The balance should be checked periodically to determine its sensitivity.

NOTE 3.—For anthracite, coke, and coal of high ash content, which do not readily burn completely, the following procedures are recommended: (a) The inside of the crucible is lined completely with ignited asbestos in a thin layer pressed well down into the angles, and the sample is then sprinkled evenly over the surface of the asbestos; or (b) the weight of the sample may be varied to obtain good ignition. If the weight is varied, it will be necessary to recalibrate the calorimeter so that the water equivalent will be based on the same temperature rise as that obtained with the new sample weight; or (c) a known amount of benzoic acid may be mixed with the sample. Proper allowance must be made for the heat of combustion of benzoic acid when determining the calorific value of the sample.

NOTE 4.—The moisture determination of the sample shall be performed simultaneously by ASTM Method D271-58, p. 1150.

**Water in Bomb.**—Add 1.0 ml. of distilled water to the bomb by a pipet. Before adding this water the bomb shall be rinsed, inverted to drain, and left undried.

**Firing Wire.**—Connect a measured length of firing wire to the ignition terminals, with enough slack to allow the firing wire to maintain contact with the sample. If cotton thread is used, connect the firing wire tautly across the ignition terminal, and tie the cotton thread around it at about the center. Arrange the ends of the cotton thread so that they are in contact with the sample. Assemble the bomb in the normal manner.

**Oxygen.**—Charge the bomb with oxygen to a consistent pressure between 20 and 30 atmospheres. This pressure must remain the same for each calibration and for each calorific determination. For the calorific value of coke, it is necessary

to use 30 atmospheres oxygen pressure. If, by accident, the oxygen introduced into the bomb should exceed the specified pressure, *do not* proceed with the combustion. Detach the filling connection and exhaust the bomb in the usual manner. Discard this sample.

The following precautions are recommended for safe calorimeter operation. Additional precautions may be found in ASTM Method E144-59T, 1961 Book of ASTM Standards, Part 8, p. 1835.

(1) The weight of coal or coke sample and the pressure of the oxygen admitted to the bomb must not exceed the bomb manufacturer's recommendations.

(2) Bomb parts should be inspected carefully after each use. Threads on the main closure should be checked frequently for wear. Cracked or significantly worn parts should be replaced. The bomb should be returned to the manufacturer occasionally for inspection and possibly proof firing.

(3) The oxygen supply cylinder should be equipped with an approved type of safety device, such as a reducing valve, in addition to the needle valve and pressure gauge used in regulating the oxygen feed to the bomb. Valves, gauges and gaskets must meet industry safety code. Suitable reducing valves and adaptors for 300 to 500 psi. discharge pressure are obtainable from commercial sources of compressed gas equipment. The pressure gauge shall be checked periodically for accuracy.

(4) During ignition of a sample, the operator must not permit any portion of his body to extend over the calorimeter.

**Calorimeter Water.**—It is preferable to adjust the calorimeter water temperature to from 1.0° to 1.4°C. (2.0° to 2.5°F.) below room temperature. Use the same weight measured to  $\pm 0.5$  g. of water in each experiment. For 2000-ml. calorimeters, the proper quantity can be obtained by use of a volumetric flask calibrated to deliver  $2000 \pm 0.5$  g. As the density of water varies with temperature, suitable corrections shall be made if the water temperature varies from the temperature at which the flask was calibrated.

**Observations.**—Transfer the bomb to the calorimeter, check that it is gas tight, and connect it to the firing circuit. Place the stirrers, thermometers, and cover in position. Start the stirrers and keep them in continuous operation throughout the determination. Stir for at least 5 minutes before reading any temperature (Note 5). Adjust the jacket temperature to match the calorimeter within  $\pm 0.01^\circ\text{C}$ . ( $0.02^\circ\text{F}$ .) and maintain for 3 minutes. Record the "initial temperature" to within one-tenth of the smallest thermometer subdivision and fire the charge. Adjust the jacket temperature to match that of the calorimeter during the period of rise, keeping the two temperatures as nearly equal as possible during the rapid rise and adjusting to within  $\pm 0.01^\circ\text{C}$ . ( $0.02^\circ\text{F}$ .) when approaching the final equilibrium temperature. Take calorimeter temperature readings at 1-minute intervals until the *same* temperature (within one-tenth of the smallest thermometer subdivision) is observed in three successive readings. Record this as the "final temperature."

**NOTE 5.**—Before taking any readings, tap the thermometer lightly and examine for mercury separation. Mercury separation will cause erroneous readings and should be corrected before proceeding. In addition, the entire thermometer should be examined daily.

**Analysis of Bomb Contents.**—Remove the bomb and release the pressure at a uniform rate, such that the operation will require not less than 1 minute. Examine the bomb interior and discard the test if unburned sample or sooty de-

posits are found. Wash the interior of the bomb with distilled water containing the titration indicator, until the washings are free of acid, and titrate the washings with standard alkali solution. Remove and measure or weigh the combined pieces of unburned firing wire, and subtract from the original length or weight to determine the wire consumed in firing. Determine the sulfur content of the sample by any of the procedures described in ASTM Method D271-58, Sections 21 through 29 (pp. 1155-1159).

**Calculations.** 9(a) *Temperature Rise*.—Using data obtained as prescribed in Section 8 for Calorimetric Water, compute the corrected temperature rise,  $t$ , as follows:

$$t = t_f - t_a$$

where  $t$  = corrected temperature rise, °C. or °F.

$t_a$  = "initial temperature" when charge was fired, corrected for thermometer error (Note 6)

$t_f$  = "final temperature," corrected for thermometer error

**NOTE 6.**—With all mercury-in-glass thermometers, it is necessary to make the following corrections if the total heat value is altered by 5.0 Btu or more. This represents a change of 0.002°F. or 0.001°C. in a calorimeter using approximately 2000 g. of water. The corrections include the calibration correction as stated on the calibration certificate, the "setting" correction for Beckmann thermometers, according to the directions furnished by the calibration authority, and the correction for emergent stem. Directions for these corrections are given in Appendix II, Section A 2, p. 1185.

(b) *Thermochemical Corrections* (Appendix II, Section A 3).—Compute the following for each test:

$e_1$  = correction for the heat of formation of nitric acid in Btu. Each milliliter of standard alkali is equivalent to 10.0 Btu

$e_2$  = correction for heat of formation of sulfuric acid, in Btu  
=  $23.7 \times$  percentage of sulfur in sample  $\times$  weight of sample in grams

$e_3$  = correction for heat of combustion of firing wire, in Btu (Note 7)  
= 4.1 Btu per cm. or 2570 Btu per g. for 34 B & S gauge Chromel C.  
= 4.9 Btu per cm. or 3150 Btu per g. for 34 B & S gauge iron wire.

**NOTE 7.**—There is no correction for platinum wire provided the ignition energy is constant.

$e_4$  = correction for heat of combustion of cotton thread (if used), in Btu. The heat supplied by the ignition of cotton thread is preferably determined by combustion in the bomb. As an alternative, it can be determined from the calorific value of cellulose, which is equivalent to 7524 Btu per g.

(c) *Calorific Value*.—Compute the gross calorific value (gross heat of combustion) by substituting into the following equation:

$$H_g = \frac{(t)(W) - e_1 - e_2 - e_3 - e_4}{g}$$

where  $H_g$  = gross calorific value, in Btu per pound

$t$  = corrected temperature rise as calculated in Section 9(a), °C. or °F., consistent with the water equivalent value

$W$  = water equivalent (see Section 6)

$e_1, e_2, e_3, e_4$  = corrections as prescribed in Section 9(b)

$g$  = weight of sample in grams

The result obtained by the above method of calculation and determination is the gross calorific value (gross heat of combustion).

Net calorific value (net heat of combustion) shall be calculated as follows:

$$H_n = H_g - 10.30 (H \times 9)$$

where  $H_n$  = net calorific value (net heat of combustion), in Btu per pound

$H_g$  = gross calorific value (gross heat of combustion) in Btu

$H$  = total hydrogen, per cent

**Precision.**—The following data shall be used for judging the acceptability of results (95% probability) on split 60-mesh pulps:

(a) *Repeatability.*—Duplicate results by the same laboratory on different days, using the same operator and equipment, should be considered suspect if they differ by more than the following amount:

Repeatability. . . . . 50 Btu, dry basis

(b) *Reproducibility.*—Results submitted by two or more laboratories (different equipment, operators, date of test, and different portions of the same pulp) should be considered suspect if they differ by more than the following amount:

Reproducibility. . . . . 100 Btu, dry basis

## APPENDIX I

### CALCULATION OF STANDARD DEVIATIONS FOR CALORIMETER STANDARDIZATION

**AI.**—The following example illustrates the method of calculating standard deviations for calorimeter standardizations:

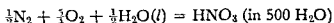
Standardiza- tion No.	Col. A Water Equivalent Btu/°C.	Col. B Code to 4400 (Col. A-4400)	Col. C (Col. B) <sup>2</sup>
1	4,412	12	144
2	4,407	7	49
3	4,415	15	225
4	4,408	8	64
5	4,404	4	16
6	4,406	6	36
7	4,409	9	81
8	4,410	10	100
9	4,412	12	144
10	4,409	9	81
Sum		92	940

$$\text{Average} = \bar{x} = \frac{\sum x}{10} = \frac{92}{10} + 4400 = 4409$$

For example, suppose the initial reading  $t_a$  was 80°F., the final reading  $t_c$  was 86°F., and that the observed stem temperature  $t^1$  was 82°F., and the calibration temperature  $t^0$  was 72°F.; then—

$$\begin{aligned}\text{Differential stem correction} &= 0.00009 (86^\circ - 80^\circ)(82^\circ - 72^\circ) \\ &= 0.005^\circ\text{F.}\end{aligned}$$

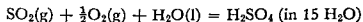
**A3. Thermochemical Corrections. Heat of Formation of Nitric Acid.**—A correction ( $e_1$ , Section 9(b)) of 10 Btu is applied for each milliliter of standard sodium carbonate solution used in the acid titration. The standard solution contains 20.90 g. of  $\text{Na}_2\text{CO}_3$  per liter. This correction is based on the assumption that (1) all the acid titrated is nitric acid formed by the following reaction:



and (2) the energy of formation of 1 mole of  $\text{HNO}_3$  in approximately 500 moles of water under bomb conditions is 14.1 kg. cal. per mole.<sup>26</sup> When sulfuric acid,  $\text{H}_2\text{SO}_4$ , is also present, part of the correction for  $\text{H}_2\text{SO}_4$  is contained in the  $e_1$  correction and the remainder in the  $e_2$  correction.

**Heat of Formation of Sulfuric Acid.**—By definition (ASTM Method D407-44, p. 1276), the gross calorific value is obtained when the product of the combustion of sulfur in the sample is  $\text{SO}_2(\text{g})$ . However, in actual bomb combustion processes, the sulfur is found as  $\text{H}_2\text{SO}_4$  in the bomb washings. A correction ( $e_2$ , Section 9(b)) of 23.7 Btu is applied for each per cent of sulfur in the 1 g. sample, which is converted to sulfuric acid. This correction is based upon the energy of formation of  $\text{H}_2\text{SO}_4$  in solutions such as will be present in the bomb at the end of a combustion. This energy is taken as -70.5 kg. cal. per mole.<sup>26</sup> A correction of  $2 \times 14.1$  per kg. cal. per mole of sulfur was applied in the  $e_1$  correction, so the additional correction necessary is  $70.5 - (2 \times 14.1) = 42.3$  kg. cal. per mole or 2370 Btu per gram of sulfur in the sample ( $23.7 \text{ Btu} \times \text{weight of sample in grams} \times \text{per cent sulfur in sample}$ ).

The value of 2370 Btu per gram of sulfur is based on a coal containing about 5% sulfur and about 5% hydrogen. The assumption is also made that the sulfuric acid is dissolved entirely in the water condensed during combustion of the sample.<sup>27</sup> If a 1-g. sample of such a fuel is burned, the resulting sulfuric acid condensed with water formed on the walls of the bomb will have a ratio of about 15 moles of water to 1 mole of sulfuric acid. For this concentration the energy of the reaction



under the conditions of the bomb process is -70.5 kg. cal. per mole.

Basing the calculation upon a sample of comparatively large sulfur content reduces the overall possible errors, because for smaller percentages of sulfur the correction is smaller.

**Fuse Wire.**—Calculate the heat in Btu contributed by burning the fuse wire in accordance with the directions furnished by the supplier of the wire. For example, the heat of combustion of 34 B & S gauge Chromel C wire is equivalent

<sup>26</sup> Calculated from data in National Bureau of Standards Circular 500.

<sup>27</sup> R. A. Mott and C. Parker, "Studies in Bomb Calorimetry IX—Formation of Sulfuric Acid," Fuel 37, 371 (1958).

position of chalybite by the phosphoric acid. For decomposition of the carbonate minerals, they suggested hydrochloric acid as the reagent which would deal adequately with all coals and cokes. Air-dried samples ground to pass a No. 60 (250-micron sieve) or, better, passing a No. 100 (149-micron) sieve if much impurity is present, are used.

**Significance of Tests.**—If solid fuel contains carbonates, the volatile matter determined according to ASTM Method D271-58<sup>31</sup> includes carbon dioxide evolved from carbonates, and the determined ash value is lower to that extent. The carbon determined in ultimate analysis represents total carbon in coal and in mineral carbonates. Therefore, an accurate determination of total carbon dioxide in mineral solid fuels is of significance for use in the correction of analytical results, in particular for correction of the volatile matter and organic values, and for calculation of coal analyses to the dry mineral matter-free basis.

### GRAVIMETRIC METHOD

The determination of  $\text{CO}_2$  is made gravimetrically by complete decomposition of carbonates present in a weighed quantity of the sample under investigation by action of 5 *N* hydrochloric acid with 1 per cent of wetting agent in a closed system, and by absorption of the liberated  $\text{CO}_2$  after purification from interfering substances, in a weighed vessel containing a reagent for carbon dioxide absorption.

**Apparatus.**—The apparatus shall consist of the following main units listed in order of passage of air:

- (a) Air-Purifying Train
- (b) Reaction Unit Assembly
- (c) Gas-Purifying Train
- (d)  $\text{CO}_2$ -Absorption Unit
- (e) An Aspiration System

The apparatus shown in Fig. 31-11 has been found most satisfactory in conforming to the requirements outlined in the section on General Considerations and proved to be advantageous when many  $\text{CO}_2$  determinations are made in coal, coke, oil shale, and other materials with a wide range of carbonate content.

NOTE 1.—The use of apparatus modified from that shown in Fig. 31-11 shall be considered permissible so long as results agree within the accepted tolerances.<sup>32</sup>

**Purity of Reagents.**—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagent of the American Chemical Society, whenever such specifications are available.<sup>33</sup> Other grades may be used, provided one first ascertains that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to the Specifications for Reagent Water (ASTM Designation: D1193).<sup>34</sup>

<sup>31</sup> Methods of Laboratory Sampling and Analysis of Coal and Coke (D271-58), 1961, Book of ASTM Standards, Part 8

<sup>32</sup> ASTM Designation: D1756 60T, Tentative Method of Test for Carbon Dioxide in Coal, 1961 Book of ASTM Standards, Part 8, p. 1284.

<sup>33</sup> Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see Reagent Chemicals and Standards, by Joseph Rosin, D. Van Nostrand Co., Inc., Princeton, N. J., and the United States Pharmacopeia.

<sup>34</sup> 1961 Book of ASTM Standards, Part 8, p. 1816.

tion of carbon dioxide is taking place. Discretion should be used in avoiding too rapid a flow which would exceed the capability of the purification train to remove interfering compounds and of the absorption tube to absorb entering  $\text{CO}_2$  completely. When the evolution of  $\text{CO}_2$  appears to have subsided, heat is applied to the reaction flask to bring the contents of it to the boiling point. To drive the reaction to completion, and to be certain that all evolved carbon dioxide is swept into the absorption tube, the contents of the reaction flask are gently boiled for approximately 30 min.

The source of heat is then removed, aspiration of air discontinued, the absorption tube disconnected from the train and weighed to the nearest 0.1 mg., taking precautions as described above. The difference in weight of the absorption tube, 7, previous to and following the liberation of carbon dioxide from the sample, represents the weight of carbon dioxide evolved.

**Calculation.**—Calculate the percentage of carbon dioxide ( $\text{CO}_2$ ) in the sample as follows:

$$\text{CO}_2, \% = \frac{A}{B} \times 100$$

where  $A$  = increase in weight of  $\text{CO}_2$  absorption tube, in grams, and  
 $B$  = grams of sample used.

#### PRESSOMETRIC METHOD <sup>39, 40, 41, 42, 43, 44</sup>

The determination of  $\text{CO}_2$  according to pressometric method is based upon measuring the change in pressure resulting from the decomposition of carbonates by action of hydrochloric acid in a calibrated system of constant volume. The mercury level in the manometer of the system is read and recorded, and the pressure increase compared with that produced by a given weight of a carbonate of known composition. The change in height of the mercury level in the manometer is directly proportional to the amount of  $\text{CO}_2$  generated in the reaction flask. The use of factor-weight of material is recommended so that 10 mm. net displacement of mercury in the calibrated manometer tube will correspond to 0.1 per cent of  $\text{CO}_2$  in the sample under investigation.

**Apparatus.**—The apparatus shall consist of the following main units:

**Reaction Unit Assembly.**

**Guard Tubes.**—Two guard tubes charged with silica gel or anhydrous magnesium perchlorate.

<sup>39</sup> A. E. Beet, Determination of Carbon Dioxide in Coals, Fuels in Science and Practice, 23, March, 1944, pp. 58–60.

<sup>40</sup> B. Entwisle and R. J. Coffey, Comparison of Methods for the Determination of Carbon Dioxide in Coal and Oil Shale, Thesis for Bachelor Chemical Engr. degree, Dept. Chemical Engineering, Ohio State University, 1951.

<sup>41</sup> E. B. Hughes, Apparatus for the Rapid Determination of  $\text{CO}_2$  Content of Raising Powders, Journal Soc. Chemical Industries (London) 61, Sept. 1942, pp. 105–106.

<sup>42</sup> ISO/TC (Secretariat-323)490, Draft ISO Proposal on Determination of Carbon Dioxide in Coal by the Pressometric Method.

<sup>43</sup> P. O. Krumin and K. Svanks, Study of Methods for the Determination of Carbonate Carbon Dioxide Content in Solid Fuels, paper presented at meeting of ASTM Committee D-5 on Coal and Coke, June, 1956; Report of Investigation, Ohio State Univ., Engineering Experiment Station, 40 pp., 1956. P. O. Krumin and K. Svanks, Four Methods of Determination of Carbon Dioxide in Solid Fuels, ASTM Bulletin No. 227, Jan., 1958, pp. 51–57.

<sup>44</sup> J. Moulson and H. C. Wilkinson, Apparatus for the Determination of Carbon Dioxide in Coal, Chemistry and Industry (London), Jan. 3, 1953, pp. 7–8.

**Reagents.** Carbon Dioxide Absorbent.—Sodium or potassium hydroxide (NaOH or KOH) impregnated on an inert carrier, No. 8 (2380-micron) to No. 20 (840-micron) mesh size.<sup>35</sup>

Hydrochloric Acid, 5 N (approximately).—Dilute 420 ml. of concentrated hydrochloric acid (HCl, sp. gr. 1.19) to 1 liter with water.

Silver Sulfate ( $\text{Ag}_2\text{SO}_4$ ) granular, or Copper Sulfate, Anhydrous ( $\text{CuSO}_4$ ) impregnated on pumice. If copper sulfate is used, crush and sieve the pumice to obtain a fraction passing the No. 6 (3360-micron) sieve and retained on the No. 20 (840-micron) sieve. Transfer 60 g. of the prepared pumice to a casserole, cover with a saturated solution of copper sulfate ( $\text{CuSO}_4$ ), evaporate to dryness with constant stirring, and then heat 3 to 4 hr. at 150 to 160°C. Cool in a desiccator and store in a glass-stoppered bottle.

Sodium Carbonate or Calcium Carbonate ( $\text{Na}_2\text{CO}_3$  or  $\text{CaCO}_3$ ).

Water Absorbent.—Anhydrous magnesium perchlorate  $\text{Mg}(\text{ClO}_4)_2$  or anhydrous calcium sulfate ( $\text{CaSO}_4$ ), passing No. 8 (2380-micron) and retained on the No. 45 (350-micron) sieve.<sup>36</sup>

Wetting Agent (10%).—Any wetting agent suitable for use in acid solution.<sup>37</sup>

**Procedure.**—When the apparatus is assembled as shown in Fig. 31-11, and made gas-tight by careful grinding, greasing, and tightening of all connections, the desired rate of air flow through the apparatus is established by regulating the screw clamp 3 (Fig. 31-11). Then the aspiration of air is discontinued by closing stop-cock, 2, the slight vacuum in the system is equalized by connecting the safety trap with atmosphere through the outlet in the bottom of the three-way stop-cock, 16a. The reaction flask, 15, is disconnected from the apparatus and into it are transferred approximately 5 g. (more or less, according to carbonate content) of air-dried sample weighed to the nearest 0.001 g. The sample in the reaction flask is then covered with 50 ml. of carbon dioxide-free distilled water, added 1% of a wetting agent, shaken vigorously to ensure a thorough wetting of the sample; then any adherent sample material is washed from the walls of the flask into the mixture using a small amount of  $\text{CO}_2$ -free distilled water, and the reaction flask is connected to the apparatus; the glass beads in the U-tube, 10, are drenched with concentrated sulfuric acid before each experiment.

In order to fill the apparatus with carbon dioxide-free air, about 1500 ml. of purified air is aspirated through the apparatus at a rate of 50 to 75 ml. per min. Then the aspiration is discontinued, the  $\text{CO}_2$ -absorption tube, 7, removed from the train, wiped off with a chamois or chemically clean, lint-free cloth, slightly damp with water<sup>38</sup> and allowed to stand for 15 min. in the balance case, weighed to the nearest 0.1 mg., and connected to the train again. Aspiration of purified air through the system is repeated for another 10 min. at the rate of 50 to 75 ml. per min., until the weight of the absorption tube is constant within 0.0003 g.

With the apparatus free of carbon dioxide and the weight of carbon dioxide absorption tube known, the analysis of the sample may be started. The aspiration system is set in operation again, and hydrochloric acid is admitted carefully from the tap funnel into the reaction flask, at such a rate that only a slow evolu-

<sup>35</sup> Ascarite, Caroxite, and Mikohbite have been found satisfactory for this purpose.

<sup>36</sup> Anhydron and Dehydrite have been found satisfactory for this purpose.

<sup>37</sup> Aerosol and Pluronic L-44 have been found satisfactory for this purpose.

<sup>38</sup> In atmosphere of low humidity (60 per cent or lower) the U-tube if rubbed with dry cotton cloth, will induce static charges. However, if a particle emitter is placed into the balance case, the troublesome static charges will be dissipated.



**Manometer.**—A glass U-tube manometer provided with adjustable scale.

**A Source of Vacuum.**

**Electric Hot Plate.**

The apparatus shown in detail in Fig. 31-12 has been found satisfactory for pressometric determination of carbon dioxide.

**Reagents.** Hydrochloric Acid, 5 N (approximately).—Dilute 420 ml. of concentrated hydrochloric acid (HCl, sp. gr. 1.19) to 1 liter with water.

Calcium Carbonate ( $\text{CaCO}_3$ ), of Anhydrous Sodium Carbonate ( $\text{Na}_2\text{CO}_3$ ).

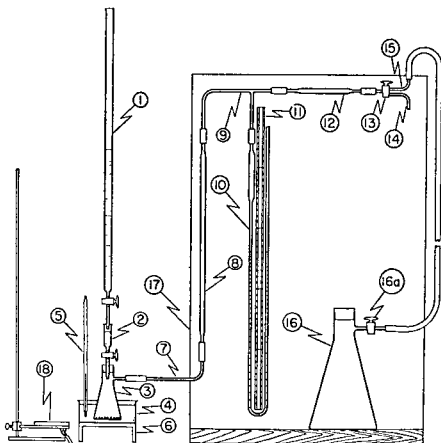


FIG. 31-12. Diagram of Apparatus for Pressometric Determination of Carbonate  $\text{CO}_2$ .

- |  |  |
|--|--|
| (1) Buret charged with 5 N HCl, with 1% wetting agent.   | (10) Manometer gage consisting of capillary U-tube of 1 mm. bore, each arm being about 45 cm. long, with the bore of one arm (connected to the T-piece) enlarged to 4 mm. over a length of 7 cm. |
| (2) Small separatory funnel charged with exactly 2 ml. of the 5 N HCl.   | (11) Adjustable scale, graduated in cm. and mm.  |
| (3) 50 ml. reaction flask, suction type of Pyrex glass with a side arm connected to the train with flexible pressure tubing. | (12) Guard tube, 10 cm. long and 5 mm. bore, charged with silica gel.  |
| (4) Water bath.  | (13) Three-way stopcock.   |
| (5) Thermometer.   | (14) Connection to the atmosphere.   |
| (6) Stand.   | (15) Connection to the vacuum.   |
| (7) Capillary tubing connected to the train with flexible pressure tubing.   | (16) Evacuated 2000 ml. suction flask, used as source of vacuum.   |
| (8) Drying tube, about 5 mm. bore and about 20 cm. long charged with silica gel.   | (17) Mounting board.   |
| (9) Capillary connecting T-piece.  | (18) Electric hot plate.   |

Silica gel, self indicating size range No. 7 (2830-micron) to No. 25 (710-micron) mesh, or Anhydrous Magnesium Perchlorate  $\text{Mg}(\text{ClO}_4)_2$ , size range No. 16 (1190-micron) to No. 30 (590-micron) mesh.

**Calibration.**—After testing for gas tightness, the apparatus must be calibrated at a specific temperature with a given weight of a carbonate of known composition in order to determine the net displacement of the mercury level. Several calibration tests should be made and the average from at least four determinations taken. The calibration tests must be repeated at frequent intervals and always when any part of the apparatus is replaced.

**Calculation of Factor-Weight To Be Taken.**—It is recommended that a factor-weight of material to be used so that 1 cm. net displacement will correspond to 0.1% of  $\text{CO}_2$  in the sample.

**Example.**—In calibrating a particular apparatus at  $23^\circ\text{C}.$ , with 0.1000 g. of powdered calcium carbonate containing 0.044 g. of  $\text{CO}_2$ , the evolved  $\text{CO}_2$  caused an average upward movement of 29.6 cm. in the mercury level of the manometer, 10 (Fig. 33-12), this value being designated as gross displacement  $x$ . A blank test using 2 ml. of acid only (no calcium carbonate), raised the mercury level 1.2 cm.,  $y$ . Thus, net displacement is  $x - y = 29.6 \text{ cm.} - 1.2 \text{ cm.} = 28.4 \text{ cm.}$  Then factor-weight in grams is calculated:

$$\frac{0.044\text{g.} \times 1 \text{ cm.}}{0.1 (x - y) \text{ cm.}} \times 100 = \frac{44}{x - y} = 1.549$$

NOTE 2.—A blank test using 2 ml. of distilled water and weight of coal equal to the approximate factor-weight shall be made in the same manner as described above, to correct the net displacement value, and consequently, the factor-weight to be taken.

**Procedure.**—Finely powdered sample (through 60 mesh or finer) is weighed to the nearest 0.001 g. and transferred into the reaction flask, 3 of Fig. 33-12, with a specific number of glass beads. The stem of the separatory funnel, 2, is filled with distilled water and the funnel with stopcock is connected to the apparatus by pushing the rubber stopper each time to a calibrated mark on the neck of the reaction flask, 3, in order to maintain constant volume of the apparatus; 5 *N* hydrochloric acid with 1% wetting agent is placed in the buret, 1. Stopcock, 13, is turned in such a position that tubing, 12, and 15, is connected. Stopcock, 16a, on the vacuum bottle, 16, is carefully manipulated so that part of the gases are withdrawn from the system, lowering the mercury in the open arm of the manometer to some predetermined position on the scale, 11. The water bath, 4, is placed in position as shown. The apparatus is permitted to stand approximately 10 min. in order for the system to reach equilibrium. The degree of equilibrium is indicated by the stability of the mercury level in the manometer, 10. One millimeter movement of the mercury in 10 min. is the maximum allowable. Then the scale which is divided into centimeters with 0.1 subdivisions is adjusted so that its zero is level with the top of the mercury meniscus.

Exactly 2 ml. of the 5 *N* HCl from the buret, 1 (Fig. 31-12), are admitted into the small separatory funnel, 2, and into reaction flask, 3, which is shaken to wet the sample thoroughly. (The reaction flask can be shaken while connected in the train because the rubber connections on both ends of the tube, 7, are flexible.) When the reaction subsides, the water bath, 4, and the stand, 6, are removed. To drive the reaction to completion, the flask and its contents are heated for 2 min. by means of an electric hot plate, 18. The contents are thus heated to between

50° and 60°C. The flask, 3, is shaken continually for 1 or 2 min., then immersed in water bath, 4, as before and the apparatus is permitted to stand for approximately 10 min. during which time equilibrium is achieved. The mercury level in the manometer is read and recorded, and the blank deducted. The temperature is recorded, and if there is notable deviation from the standard temperature a correction is applied. The corrected net reading in decimeters gives the percentage of  $\text{CO}_2$  in the sample under investigation.

**Precision.**—The following permissible differences in results should be used for judging the acceptability of results: <sup>45</sup>

Carbon Dioxide, %	Repeatability (Same Laboratory), %		Reproducibility (Different Laboratories), %	
Under 1.0	0.05		0.10	
Over 1.0	0.10		0.20	

## THE DETERMINATION OF FORMS OF SULFUR IN COAL <sup>46, 47, 48, 49, 50, 51, 52</sup>

**Occurrence of Sulfur.**—Sulfur does not occur as such in coal but is invariably present in organic compounds along with the coal substance, because of the fact that coal-forming vegetation contains both protein and non-protein sulfur. In addition, forms of sulfur occur in coals as impurities in inorganic combinations, mainly as sulfides of iron (pyritic or markasite,  $\text{FeS}_2$ ); a small amount of sulfur, especially in weathered coals, occurs also as sulfates, generally as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ); and sometimes also as ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ).

These forms of sulfur are commonly referred to as sulfate-, pyritic-, and organic-sulfur.

**Scope.**—This method of test covers procedures for the gravimetric determination of sulfate sulfur in the hydrochloric acid extract of the coal sample, and the indirect determination of pyritic sulfur by determining, titrimetrically, the iron combined in the pyritic state, employing the nitric acid extract of the coal sample. The organic sulfur is calculated by the deduction of sulfate- and pyritic-sulfur from the total sulfur.

**Summary of Method.**—An essential feature of these methods is extraction of sulfate- and pyritic-sulfur from a weighed quantity of air-dried coal pulverized to pass a No. 60 (250-micron) sieve by treatment with diluted acids.

<sup>45</sup> ASTM Designation: D1756-60T, 1961 Book of ASTM Standards, Part 8, p. 1287.

<sup>46</sup> Edwards, A. H., Daybell, G. N., and Pringle, W. J. S., An Investigation into Methods for the Determination of Forms of Sulfur in Coal, Fuel, 37, 47-61, Jan. 1958.

<sup>47</sup> ISO Recommendation No. 157—Determination of Forms of Sulfur in Coal, 1961.

<sup>48</sup> Krumin, Peter O., The Meigs Creek No. 9 Coal Bed in Ohio, Part III—Further Study of the Chemical and Physical Properties, and Washability Characteristics, with a Brief Review of New Methods Employed, OSU, Engng. Expt. Sta. Bull., 165, 47-51, July, 1957.

<sup>49</sup> Krumin, P. O., Interlaboratory Study of Methods for the Determination of Total Sulfur, Forms of Sulfur, and Chlorine in Coal, pap. to Ann. Meet. ASTM D-5, June, 1959; R. I. Ohio State Univ. Engng. Expt. Sta., June, 1959, 55 pp.

<sup>50</sup> Mott, R. A., Rapid Determination of Forms of Sulfur in Coal (Brit. Coke Res. Association, Panel No. 1, Third Rept. to Res. Comm., July 1949, 13 pp.); Fuel, 29, 53-61, Mar. 1950.

<sup>51</sup> Mott, R. A., Rapid Determination of Pyritic and Sulphate Sulphur in Coals, Gas. J., 264, 44, Oct. 4, 1950.

<sup>52</sup> Teichmann, R. F. J., The Oxidation of Pyrites Associated with African Coals, J. Chem. Met. and Mining (Soc. of S. Africa) XLV (7 and 8) 141-156, Jan.-Feb. 1954.

The sulfate-sulfur is extracted from a sample of coal with diluted hydrochloric acid and determined in the extract gravimetrically as  $\text{BaSO}_4$ . In addition, the iron content of the extract is also determined for use in the calculation of pyritic sulfur.

The pyritic sulfur minerals, being insoluble in dilute hydrochloric acid, are quantitatively dissolved by dilute nitric acid under the experimental conditions, employing another portion of the sample. Since the nitric acid dissolves pyritic-sulfur, plus hydrochloric acid soluble sulfate-sulfur compounds, and a small portion of the organic-sulfur from some coal, the sulfur content of this extract is not a reliable measure of the pyritic-sulfur, even after correction for sulfate-sulfur. Therefore, the determination of pyritic sulfur is carried out indirectly in the nitric acid extract. The pyritic-sulfur is conveniently obtained by determining the amount of iron combined in pyritic state, which is equal to the difference between nitric acid and hydrochloric acid soluble iron; and the pyritic-sulfur calculated from stoichiometric formula  $\text{FeS}_2$ .

NOTE.—An alternative procedure may be used, according to which the two acid extractions are carried out on the same portion of the coal sample under investigation, the nitric acid treatment being applied to the coal residue from the hydrochloric acid extraction for determination of sulfate-sulfur. In this case, the determination of iron in the hydrochloric acid extract is unnecessary, because the iron determined in nitric acid extract represents the pyritic iron. However, there are several objections: for example, if the percentage of pyritic iron in coal is high, a 5-g. sample of coal, as required for the determination of usually low sulfate-sulfur content, would cause difficulties in handling relatively large amounts of pyritic iron and would require the use of an aliquot; the determination of pyritic iron is delayed until the extraction of sulfate-sulfur is completed.

**Significance.**—Early investigators considered only the total sulfur content in coal because of the necessity of knowing it as a factor for correction in the calorimetric determination of heat of combustion. However, the behavior of the individual forms in which sulfur occurs in coal is of prime importance in coal preparation, storage, and various uses of coal. The amount of individual forms of sulfur must be known for coal analysis, particularly for calculation of analysis data to mineral matter-free basis. Consequently, to know the total amount of sulfur in coal, as well as the forms in which sulfur occurs in run-of-mine and in marketable coal is of great significance.

**Apparatus.** Cold Finger Condenser (Fig. 31-13).

**Crucibles.**—Porcelain, platinum, alundum, or silica crucibles of 10–15-ml. capacity, shall be used for igniting  $\text{BaSO}_4$ .

**Hot Plate.**—Electrically heated hot plate, with full temperature control which permits adjustment of surface temperatures.

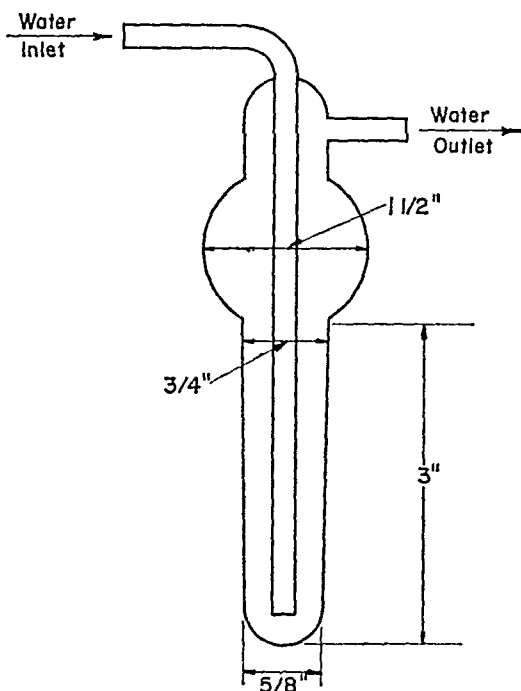


FIG. 31-13. Cold Finger Condenser for Use in the Determination of Forms of Sulfur.

**Muffle Furnace.**—Electrically heated muffle furnace with a substantially uniform hot zone at  $800^{\circ}\text{C} \pm 25^{\circ}\text{C}$ .

**Mechanical Shaking Machine.**

**Purity of Reagents.**—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>53</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit the use without lessening the accuracy of the determination.

Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to the Specifications for Reagent Water (ASTM Designation: D1193).<sup>54</sup>

**Reagents.** Ammonium Hydroxide, 18 *N*.—Ammonium hydroxide ( $\text{NH}_4\text{OH}$ , sp. gr. 0.880).

**Ammonium Thiocyanate Solution (100 g. per liter).**—Dissolve 100 g. ammonium thiocyanate ( $\text{NH}_4\text{CNS}$ ) crystals in water, filter, and dilute the clear filtrate to 1 liter.

**Barium Chloride Solution (100 g. per liter).**—Dissolve 100 g. barium chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) in 1 liter water.

**Hydrochloric Acid, 11 to 12 *N*.**—Concentrated hydrochloric acid ( $\text{HCl}$ , sp. gr. 1.19).

**Hydrochloric Acid, 5 *N*.**—Dilute 420 ml. concentrated hydrochloric acid ( $\text{HCl}$ ) to 1 liter with water.

**Hydrochloric Acid, 0.5 *N*.**—Dilute 42 ml. concentrated hydrochloric acid ( $\text{HCl}$ ) to 1 liter with water.

**Hydrogen Peroxide.**—Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) 30% weight/volume.

**Methyl Orange Indicator Solution.**—Dissolve 0.02 g. methyl orange in 100 ml. hot water and filter.

**Nitric Acid, 2 *N*.**—Dilute 125 ml. concentrated nitric acid ( $\text{HNO}_3$  sp. gr. 1.42) to 1 liter with water.

**Standard Blank Solution.**—Dissolve 0.600 g. potassium sulfate ( $\text{K}_2\text{SO}_4$ ) in water and make up to 1000-ml. solution.

**Standardized Titanous Chloride Solution, 0.06 *N* (approximately).**—Dilute 50 ml. commercially available 20% titanous chloride solution to 1000 ml. with hydrochloric acid (5:95), and accurately standardize against a primary standard.

**Standardization Procedure for Titanous Chloride.**—(a) Preparation of Standard Iron Solution (1 ml. = 0.001 g. Fe). Weigh accurately 1.0000 g. iron of known composition, transfer into a 250-ml. beaker and dissolve in 50 ml. of hydrochloric acid (1:1). (See Note.) Oxidize with hydrogen peroxide (30%), adding a few drops in excess, and boil for 30 minutes. Add 25 ml. of hydrochloric acid, cool, and dilute to 1 liter in a volumetric flask.

(b) Standardization.—Pipet a 100-ml. portion of standard iron solution (a) into a 500-ml. Erlenmeyer flask; add 150 ml. of hydrochloric acid (5:95) and 10 ml. of ammonium thiocyanate solution (10:90), and titrate with  $\text{TiCl}_3$  to a complete loss of color. When nearing the end of the titration, add the  $\text{TiCl}_3$  solution dropwise

<sup>53</sup> Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see Reagent Chemicals and Standards, by Joseph Rosin, D. Van Nostrand Co., Inc., Princeton, N. J., and the United States Pharmacopeia.

<sup>54</sup> 1961 Book of ASTM Standards, Part 8, p. 1816.

and swirl the contents for approximately one minute (avoiding shaking of air bubbles into the solution) before adding the next drop.

$$\text{Normality of TiCl}_3 \text{ solution} = \frac{A}{B} \times 0.017905,$$

where  $A$  = milliliters of standard iron solution, and

$B$  = milliliters of  $\text{TiCl}_3$  solution required to titrate the standard iron solution.

$$\text{Factor } 0.017905 = \frac{1000}{55.85} \times 0.001$$

(55.85 g. Fe are equivalent to 1000 ml. of 1  $N$   $\text{TiCl}_3$ ; 1 ml. of standard iron solution = 0.001 g. Fe)

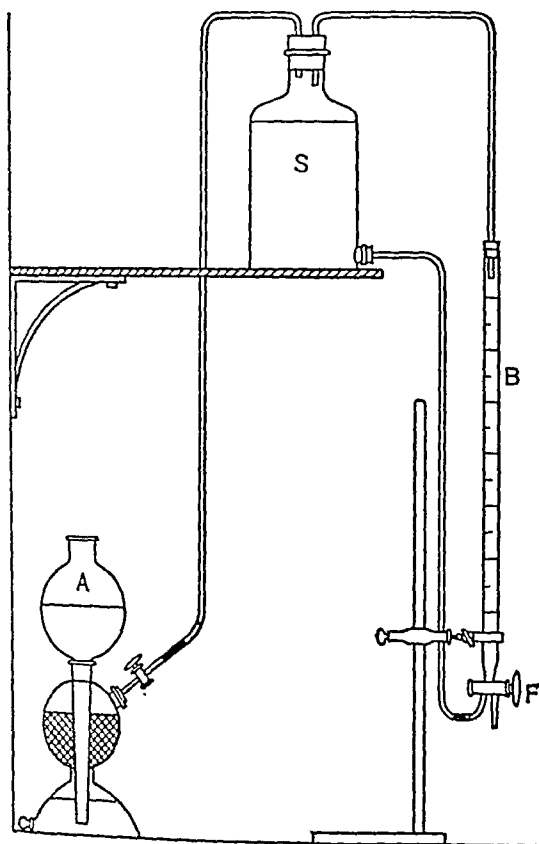


FIG. 31-14. Apparatus for Storage of Titanous Chloride Solution under an Atmosphere of Hydrogen. (Pour the titanous chloride solution prepared as described above into the storage bottle (S) until the bottle is practically overflowing. Place in position the rubber stopper carrying the tube to the buret (B) and the hydrogen inlet tube, thus displacing a quantity of solution. With the hydrogen supply from the Kipp generator (K) turned on, remove all air from tubes and fill all spaces with hydrogen from the generator by properly manipulating the three-way stopcock (F). Maintain an atmosphere of hydrogen over the solution during storage.)

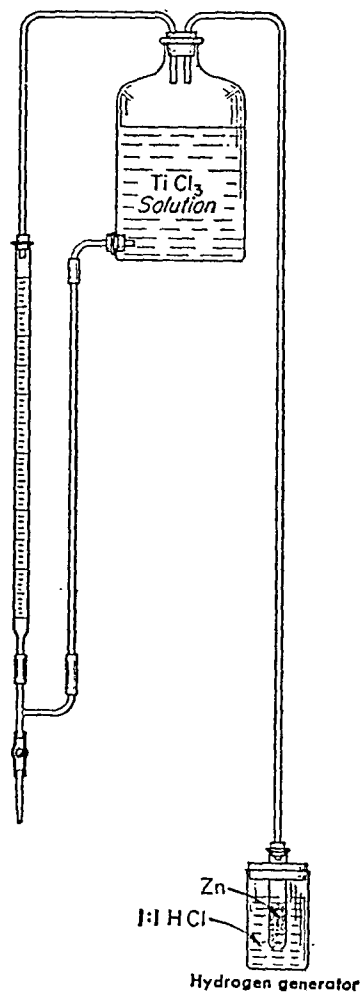


FIG. 31-15. Apparatus for Storage of Titanous Chloride Solution under an Atmosphere of Hydrogen.

NOTE.—National Bureau of Standards standard sample No. 55d of ingot iron is satisfactory for this purpose.

*Storage of Standardized Titanous Chloride Solution.*—The titanous chloride standard solution must be protected from direct sunlight and contact with air, because it is easily oxidized. This little inconvenience is required as a precaution and is well justified, because titanous chloride is a powerful reducing agent and very useful for the direct titration of ferric iron.

The titanous chloride standard solution can be stored in an atmosphere of hydrogen over the solution during two months or even longer with no appreciable change, employing apparatus as shown in Figs. 31-14 or 31-15. The normality, however, should be checked at fairly frequent intervals.

#### DETERMINATION OF SULFATE SULFUR

Obtain a laboratory sample prepared according to ASTM Designation: D271-58 (p. 1145).

*Extraction of Sulfate Sulfur.*—Before commencing the determination, mix the sample thoroughly, preferably by mechanical means. Weigh accurately about 5 g. air-dried coal ground to pass a 60-mesh (250-micron) sieve, transfer it into a 250-ml. Erlenmeyer flask, add carefully 25 ml. of 5 *N* hydrochloric acid, and close with a rubber stopper after indications of the evolution of gases cease. Shake the flask on a mechanical shaking machine (5 to 10 minutes) until the coal is thoroughly wetted, then add another 25 ml. of 5 *N* hydrochloric acid, washing the coal from the stopper and from the sides of the flask. Fit a cold finger condenser (Fig. 31-13) into the neck of the flask and place on hot plate. Boil for 30 minutes, rinse the cold finger condenser with dilute hydrochloric acid, and filter the contents of the flask through a medium-textured double acid-washed filter paper into 400 ml. beaker. Transfer the residue to the filter, wash six times with the dilute hydrochloric acid, using a total quantity of about 20 ml., and discard the residual coal left on the filter paper. Determine, in the filtrate, the sulfur and the iron (representing hydrochloric acid soluble iron).

*Separation of Sulfur and Iron.*—Add 2 to 10 ml. of saturated bromine water to the filtrate, boil the mixture for 5 minutes to ensure that all the iron is in the ferric state, and to expel the excess bromine. Precipitate the iron by adding cautiously ammonium hydroxide in a slow stream until a slight excess is present, and add 5 ml. in excess, constantly stirring to coagulate the ferric hydroxide. Place covered beaker on the hot plate and boil for 1 minute. Then filter the liquid (employing glass funnels with well-fitted, ashless, medium-texture 11-cm. filter paper) into a 600-ml. beaker. Wash the precipitate several times with hot water to which has been added a trace of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ . Retain the filtrate for the determination of sulfur, and the precipitate with the original beaker for the determination of non-pyritic iron.

NOTE.—If a relatively large amount of iron is present, dissolve the iron in the original beaker and reprecipitate; add the filtrate from the second precipitation directly to the first filtrate, and determine the sulfur in it.

*Determination of Sulfate Sulfur.*—Neutralize the filtrates from the precipitation of ferric hydroxide with concentrated hydrochloric acid and add an excess of about 1 ml., employing methyl orange as indicator. Heat the solution to boiling and add dropwise, with stirring, 10 ml. of 10% barium chloride. Complete the gravimetric determination of sulfur according to ASTM Designation: D271-58 (p. 1156).

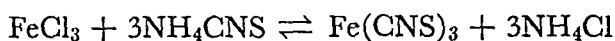
The sulfur determined in the filtrate represents the sulfur combined as sulfate in the coal.

**Blank.**—Carry out a blank determination under the same conditions but omit the coal. Pipet 10 ml. of the standard sulfate solution to the filtrate before adding the methyl orange indicator. The weight of the barium sulfate found in the blank determination, less the equivalent of the standard solution, is deducted from that obtained in the full determination.

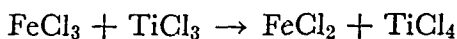
**Determination of Non-Pyritic Iron.**—Dissolve the iron precipitate from the filter paper with 120 ml. of hot hydrochloric acid (10:90), collect the filtrate into original beaker used for precipitation of the iron, and loosen traces of precipitate from the walls of the beaker by a glass rod tipped with a rubber policeman. Rinse the filter paper with 120 ml. hot water, cool the filtrate, and add to it 25 ml. of 10% ammonium thiocyanate solution as an internal indicator and determine the iron in cold solution by titration with approximately 0.06 *N* standardized titanous chloride. (See Note.)

**NOTE.**—Alternative titrimetric methods for the determination of iron are permissible, provided that the results obtained by these methods will lay within the established limits of tolerances.

When ammonium thiocyanate is added to a ferric chloride solution blood-red thiocyanate is formed.



Ferric chloride reacts with titanium trichloride to give ferrous chloride and titanium tetrachloride:



The end point is reached when complete loss of color takes place.

**Blank.**—Make a blank determination, following the same procedure and using the same amounts of all reagents.

Record the volume (ml.) of titanous chloride solution required for titration of sample, subtract the volume (ml.) required for blank, and use the difference in calculation of pyritic iron.

## DETERMINATION OF PYRITIC SULFUR-INDIRECT

**Extraction of Pyritic Iron.**—Before commencing the determinations, mix the sample thoroughly, preferably by mechanical means.

Weigh accurately about 1 g. air-dried coal, ground to pass a 60-mesh (250-micron) sieve and transfer into a 250-ml. Erlenmeyer flask; add 25 ml. of the 2 *N* nitric acid and close with a stopper after indication of the evolution of gases ceases. Shake the flask in a mechanical shaking machine until the coal is thoroughly wetted (5 to 10 minutes), then rinse the coal from the stopper and the walls of the flask with another 25 ml. of 2 *N* nitric acid; place a cold finger condenser (Fig. 31-13) into the neck of the flask and boil for 30 minutes. Then rinse the cold glass finger with 2 *N* nitric acid, and filter the contents through a medium textured double acid-washed filter paper into a 600-ml. beaker, wash six times with the 2 *N* nitric acid, and discard the residual coal left on the filter paper. Retain the filtrate for determination of iron.

Add to the filtrate 2 ml. of 30% hydrogen peroxide and boil for 5 minutes to destroy any coloration arising from the decomposition of the coal.



**Separation of Iron.**—Heat the filtrate to boiling point, precipitate the iron by adding the ammonium hydroxide in a slow stream until a slight excess is present, constantly stirring to coagulate the ferric hydroxide. Place the covered beaker on the hot plate and boil for 1 minute. Filter through an ashless, medium-textured filter paper into a beaker, and wash the precipitate several times with hot water to which has been added a trace of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ . Retain the precipitate with original beaker, for determination of iron.

Dissolve the iron precipitate on filter paper with 25 to 30 ml. of hot 5 *N* hydrochloric acid, wash filter six times with hot (10:90) hydrochloric acid, collect the filtrate into original beaker used for precipitation of the iron, and loosen the traces of precipitate from the walls of the beaker by a glass rod tipped with a policeman.

Reprecipitate the iron in the filtrate as before, and filter.

#### DETERMINATION OF PYRITIC IRON—TITANOUS CHLORIDE METHOD

**Procedure.**—Dissolve the iron precipitate, and determine the iron in cold solution by titration with titanous chloride as described in the preceding section.

The amount of iron so determined represents both the pyritic and the hydrochloric acid soluble iron in coal. The pyritic iron is the difference between the amounts of iron determined in the two extracts.

**Blank.**—Make a blank determination, following the same procedure and using the same amounts of all reagents employed in the regular determination, and correct the volume (ml.) of titanous chloride required for titration of the sample by subtracting the volume (ml.) used in titration of the blank.

**Calculation.**—Calculate the pyritic-sulfur content as follows:

$$\text{Pyritic-sulfur, per cent by weight} = \left( \frac{A}{w} - \frac{B}{W} \right) N \times 6.412$$

where *A* = milliliters of  $\text{TiCl}_3$  solution required for the titration of iron of the nitric acid extract, after subtraction of the blank value,

*B* = milliliters of  $\text{TiCl}_3$  solution required for titration of iron of the hydrochloric acid extract, after subtraction of the blank value,

*w* = weight (g.) of sample used in nitric acid extraction,

*W* = weight (g.) of sample used in hydrochloric extraction, and

*N* = normality of the  $\text{TiCl}_3$  solution (1 ml. 0.1 *N*  $\text{TiCl}_3$  solution = 0.005585 g.

Fe), and factor  $6.412 = \left( 0.05585 \times \frac{\text{S}_2}{\text{Fe}} \right) \times 100 = 5.585 \times 1.1481$ .

#### ALTERNATIVE FOR THE DETERMINATION OF IRON BY THE STANNOUS CHLORIDE—POTASSIUM DICHROMATE METHOD<sup>55</sup>

**Reagents.** Stannous Chloride Solution (50 g. per liter).—Dissolve 5 g. of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 10 ml. of  $\text{HCl}$  and dilute to 100 ml. with water. Prepare this solution freshly before use.

**Mercuric Chloride Solution (saturated).**—Dissolve 8 g. of  $\text{HgCl}_2$  in 100 milliliters of hot water, cool to room temperature, and filter.

**Sulfuric-Phosphoric Acid Mixture.**—Slowly add 150 ml. of  $\text{H}_2\text{SO}_4$  and 150 ml. of  $\text{H}_3\text{PO}_4$  (85%) to 700 ml. of cold water, while stirring constantly.

<sup>55</sup> For further information concerning the determination of iron by this method, see 1956 Book of ASTM Methods for Chemical Analysis of Metals.

**Sodium Diphenylamine Sulfonate Indicator Solution (2 g. per liter).**—*Method A* (Preparation from Barium Diphenylamine Sulfonate).—Dissolve 0.32 g. of barium diphenylamine sulfonate in 100 ml. of hot water. Add 0.5 g. of  $\text{Na}_2\text{SO}_4$ , stir, and filter off the precipitate of  $\text{BaSO}_4$ . Store in a dark-colored bottle.

*Method B* (Preparation from Sodium Diphenylamine Sulfonate).—Dissolve 0.20 g. of sodium diphenylamine sulfonate in 100 ml. of water. Store in a dark-colored bottle.

**Standard Potassium Dichromate Solution (0.1 N).**—Twice recrystallize  $\text{K}_2\text{Cr}_2\text{O}_7$  from water. Dry the crystals at  $110^\circ\text{C}$ ., pulverize, and dry at  $180^\circ\text{C}$ . to constant weight. Dissolve 4.9035 g. of the  $\text{K}_2\text{Cr}_2\text{O}_7$  in water and dilute to 1 liter in a volumetric flask.

*Standardization.*—This is a primary standard.

**NOTE.**—National Bureau of Standards oxidimetric standard sample No. 136 of  $\text{K}_2\text{Cr}_2\text{O}_7$  is satisfactory for this purpose.

*Procedure.*—Dissolve the iron precipitate retained as described in the section on Separation of Sulfur and Iron (p. 1198), and the section on the Separation of Iron (p. 1200) with 15 to 25 ml. of hot  $\text{HCl}$  (1:4) and wash the filter thoroughly with hot water. Heat the solution to boiling. Add  $\text{SnCl}_2$  solution drop by drop, while stirring, until the color of the ferric iron is discharged, and then add 1 or 2 drops more. Wash down the inside of the beaker and quickly cool the solution to room temperature. Add, all at once, 10 ml. of saturated  $\text{HgCl}_2$  solution, stir, again wash down the inside of the beaker, and allow the solution to stand for 2 to 3 minutes. Add 15 ml. of the  $\text{H}_2\text{SO}_4$ — $\text{H}_3\text{PO}_4$  mixture and 2 to 3 drops of sodium diphenylamine sulfonate indicator, and dilute to about 200 ml. Titrate slowly with 0.1 N  $\text{K}_2\text{Cr}_2\text{O}_7$ . As the end point is approached, the color deepens to a blue green, which changes to a purple or violet blue on the addition of 1 drop of  $\text{K}_2\text{Cr}_2\text{O}_7$ . The titration should be finished deliberately, as it takes a few seconds to obtain the permanent end point color.

*Blank.*—Make a blank determination, following the same procedure and using the same amounts of all reagents.

**NOTE.**—Ferric iron must be present in the solution in order to obtain the purple or violet-blue end point color. If the color fails to form, the blank is less than the equivalent of 1 drop of 0.02 N  $\text{FeSO}_4$ , as this contains sufficient iron to yield an end point.

*Calculation.*—Calculate the percentage of iron as follows:

$$\text{Iron, \% by weight} = \frac{(A - B)C}{D} \times 5.585$$

where  $A$  = milliliters of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution required for titration of the sample,  
 $B$  = milliliters of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution required for titration of the blank,  
 $C$  = Normality of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, and  
 $D$  = grams of sample used.

(1 ml. 1 N  $\text{K}_2\text{Cr}_2\text{O}_7$  solution = 0.05585 g. Fe)

### ORGANIC SULFUR

The percentage of organic sulfur in the coal is obtained by subtracting the sum of the sulfate and pyritic-sulfur from the percentage of total sulfur in the coal

obtained in a separate determination by the Eschka or other standard methods, according to ASTM Designation: D271-58 (p. 1155).

### TOLERANCES

The results of duplicate determinations carried out at different times on the same sample in the same laboratory by the same operator using the same apparatus should not differ more than:

Sulfate sulfur . . . . .	0.02
Pyritic sulfur, under 2% . . . . .	0.05
Pyritic sulfur, 2% or more . . . . .	0.10

The means of the results of duplicate determinations carried out by different laboratories on representative samples taken from the same bulk sample after the last stage of reduction should not differ more than:

Sulfate sulfur . . . . .	0.03
Pyritic sulfur, under 2% . . . . .	0.10
Pyritic sulfur, 2% or more . . . . .	0.20

### SULFUR IN COAL ASH <sup>56</sup>

This method of test covers the gravimetric determination of sulfur in the coal ash obtained from tests in accordance with Section 13 and 14 of the Methods of Laboratory Sampling and Analysis of Coal and Coke (ASTM Designation: D271, p. 1151).

**Apparatus.** Crucibles with Lids, platinum, 30-ml.

Crucibles, porcelain, platinum, alundum, or silica, low-form, 10 to 15 ml.

Muffle Furnace, electric, capable of reaching a temperature of 950°C.

**Purity of Reagents.**—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>57</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to the Specifications for Reagent Water (ASTM Designation: D1193).

**Reagents.** Barium Chloride Solution (100 g. per liter).—Dissolve 100 g. of barium chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) in water and dilute to 1 liter.

**Hydrochloric Acid (1:1).**—Mix 1 volume of concentrated hydrochloric acid ( $\text{HCl}$ , sp. gr. 1.19) with 1 volume of water.

**Methyl Orange Indicator Solution (0.20 g. per liter).**—Dissolve 0.02 g. of methyl orange in 100 ml. of water and filter.

<sup>56</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as D1757-60T.

<sup>57</sup> Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see Reagent Chemicals and Standards, by Joseph Rosin, D. Van Nostrand Co., Inc., Princeton, N. J., and the United States Pharmacopeia.

by G. N. Daybell and W. J. S. Pringle,<sup>58</sup> confirm reports made by early investigators that only part of the chlorine in coal can be removed by extraction with water, indicating that only part can be present as sodium chloride. They established also that potassium-, calcium-, and magnesium-chlorides are not present in significant amounts in the British coals used for investigation, and that a considerable part of chlorine is present not as metal chlorides, but as chloride ions attached to the coal substance by a linkage with ion-exchange properties. The coals examined by Daybell and Pringle contained water-soluble sodium equivalent to one third to one half (30% to 54%) of the total chlorine content, indicating to what extent chlorine compounds can be removed in a cleaning process employing water.

In addition to the chlorine compounds present in coal seams, chlorides may be introduced into coals during wet cleaning if the water contains substantial amounts of chlorides. They may also be introduced by treating marketable coal with calcium chloride solution to dustproof and to mitigate the problem of freezing in shipment.

*Scope and Summary of the Method.*—This method of test covers procedures for the titrimetric determination of total chlorine extracted from the combustion residue of the coal sample. The combustible matter in coal is removed and the chlorine is retained as soluble alkali chlorides, by combustion of the test sample in the presence of Eschka mixture, either in calorimetric bomb, or by incineration in a muffle furnace at  $775^{\circ} \pm 25^{\circ}\text{C}$ .

#### DETERMINATION OF CHLORINE IN COAL BY THE BOMB-COMBUSTION METHOD<sup>59, 60, 61</sup>

All the chlorine in the coal sample is released by combustion in a calorimetric bomb, containing oxygen under pressure. The chlorine thus released is absorbed in an ammonium carbonate solution, and the amount of chlorides present in the bomb washings is determined by titration with thiocyanate in a nitric acid solution containing silver and trivalent iron (Charpenter-Volhard method).

*Significance of Test for Chlorine.*—Because the amount of chlorine compounds in American coal is, in general, considerably smaller than in European coals, the determination of chlorine has not been considered of interest to consumers in the United States, and therefore was neglected by early investigators. However, at the present time, because of the effect of chlorine in coal use, the significance of knowing the chlorine content is widely recognized as being essential for the proper utilization of coal.

In industrial use of coal at high temperatures, the chlorine compounds are volatilized, causing considerable damage to appliances with which these products

<sup>58</sup> Daybell, G. N., and Pringle, W. J. S., The Mode of Occurrence of Chlorine in Coal. *Fuel*, 37, 283-292, 1958.

<sup>59</sup> ISO/TC 27 (Secretariat-361) 530E, Determination of Chlorine in Coal by the Bomb-Combustion Method, Draft ISO Recommendation N 210 (Revised March, 1961); ISO/TC 27 (Secretariat-383) 552, June, 1961.

<sup>60</sup> For further information concerning the experimental work see: P. O. Krumin, Inter-laboratory Study of Methods for the Determination of Total Sulfur, Forms of Sulfur, and Chlorine in Coal, pap. to Ann. Meet. ASTM D-5, June, 1959, 55 pp.; and The Third Inter-laboratory Study of Methods for the Determination of Total Sulfur, Forms of Sulfur, and Chlorine in Coal, pap. to Ann. Meet. ASTM D-5, Section XXI-B, June 28, 1960, 41 pp.

<sup>61</sup> Moszynski, Z. K., Chlorine by the Bomb Method, *J. Appl. Chem.*, 5, 168-70, 1935.

come in contact. They also contribute to the formation of deposits on boiler tubes in steam-raising plants. For example, A. W. Williams<sup>62</sup> reports that in a survey of 28 power stations using stoker-fired coals with more than 0.15% chlorine content, all gave the main cause of boiler trouble as bonded deposits on the tubes, necessitating lengthy removal operations.

At the temperatures prevailing at manufactured-gas plants and coal-carbonization plants, chlorides penetrate brick work and undergo fusion to form a compound of sodium, aluminum, and silicon which causes the brick to crack and fall away. The hydrochloric acid and ammonium chlorides, present in the gases evolved, cause severe corrosion of the by-product plant. H. F. Yancey and M. R. Geer<sup>63</sup> have called attention to the pertinent publications, and have outlined the effect of chlorine in coal as follows: "When coals containing more than about 0.05% sodium chloride are coked, the refractory lining of the ovens, unless made of silica, suffers from corrosion, often so severely that the lining must be replaced after a few months of use. Silica bricks are more resistant than fire-clay bricks to such attack."

**Apparatus. Combustion Bomb.**—A calorimetric bomb of 300-ml. ( $\pm 50$ -ml.) capacity, made of material unaffected by the combustion process or products, shall be provided with the usual fittings for ignition as in the determination of calorific value. Materials used in the bomb assembly, such as the head gasket and lead-wire insulation, shall be resistant to heat and chemical action, and shall not undergo any reaction which will affect the chlorine content of the liquid in the bomb.

**Crucible.**—Sample crucible, nickel-chromium or silica, approximately 25-mm. diameter and 20-mm. height.

**Firing Wire.**—Fuse wire, Fe-Ni-Cr alloy, approximately No. 34 gauge as used for oxygen bombs, or platinum wire.

**Ignition Circuit.**—Ignition circuit capable of supplying sufficient current to ignite the sample, the nylon thread, or the dry cotton wicking without melting the platinum wire.

**Metal Vessel.**—A cylindrical metal vessel to enable the bomb to be fully immersed when approximately 2 liters of water are added.

Nylon sewing or cotton wicking, white for optional use with platinum wire.

**Purity of Reagents.**—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>64</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit the use without lessening the accuracy of the determination.

Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to the Specifications for Reagent Water (ASTM Designation: D1193).<sup>65</sup>

<sup>62</sup> Williams, A. Wyn, *Coal Manual for Industry*, Book Division, Conover-Mast Publications, Inc., New York, Chicago, 1952, 324 pp.

<sup>63</sup> Yancey, H. F., and Geer, M. R., *The Cleaning of Coal*, in *Chemistry of Coal Utilization*, H. H. Lowry, ed., John Wiley and Sons, Inc., New York, 1, 1950, p. 588.

<sup>64</sup> Reagent Chemicals, American Chemical Society Specifications, Am. Chem. Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Reagent Chemicals and Standards*, by Joseph Rosin, D. Van Nostrand Co., Inc., Princeton, N. J., and the United States Pharmacopeia.

<sup>65</sup> 1961 Book of ASTM Standards, Part 8, p. 1816.

**Reagents. Ammonium Carbonate Solution.**—Dissolve approximately 10 g. of ammonium carbonate,  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$  in 100 ml. water; freshly prepared solution shall be used.

**Ferric Ammonium Sulfate Indicator Solution.**—Add sufficient nitric acid to a cold saturated solution of ferric ammonium sulfate  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  to remove the brown color.

**Eschka Mixture.**—Thoroughly mix two parts by weight of light calcined magnesium oxide ( $\text{MgO}$ ) and one part of anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). Both materials should be as pure as possible and have a very low chlorine content.

**Nitric Acid (1:1).**—Mix equal volumes of concentrated nitric acid ( $\text{HNO}_3$ , sp. gr. 1.42, and free from the lower oxides of nitrogen) and water.

Nitrobenzene ( $\text{C}_6\text{H}_5\text{NO}_2$ ), analytical reagent quality (light color).

**Oxygen.**—The oxygen used for combustion shall be free of combustible material and halogen compounds available at pressure of 40 atmospheres.

**Potassium Thiocyanate Solution (approximately 0.025 N).**—Dissolve about 3 g. of potassium thiocyanate ( $\text{KCNS}$ ) in 1000 ml. water, and standardize against silver nitrate solution.

**Silver Nitrate Solution 0.025 N.**—Dissolve 4.2473 g. dry, crushed, crystalline silver nitrate ( $\text{AgNO}_3$ , dried at  $125^\circ\text{C}$ . for 2 to 3 hours) in a small quantity of water, and add water up to 1000 ml.

**Procedure. Extraction of Chlorine.**—Before commencing the determination, mix the sample thoroughly for at least 1 minute, preferably by mechanical means. Weigh accurately about 1 g. air-dried coal, ground to pass a 60-mesh sieve, and mix intimately with 1 g. Eschka mixture in a porcelain basin, and then transfer to the sample crucible.

Cut a piece of firing wire, (Fe-Ni-Cr alloy, or platinum) of about 100 mm. length, coil the middle section (about 20-mm.), and attach the free ends to the terminals. If thread is used, arrange the coil so that it will be above and to one side of the sample crucible. Attach to the coil a nylon thread, or wisp of cotton, of such length that one end will extend into the sample crucible, and thereby provide a means for igniting the sample. Place about 5 ml. ammonium carbonate solution in the bomb and, by means of a rubber policeman, wet the interior surface of the bomb, including the head, as thoroughly as possible. Place the sample crucible in position and arrange the thread so that the end dips into the sample. Assemble the bomb and tighten the cover securely.

Admit oxygen slowly (to avoid blowing coal from the crucible) until a pressure of 25 atmospheres is reached. Immerse the bomb in a cold water bath, connect the open electrical circuit, and close the circuit to ignite the sample. The bomb shall stand in the water bath for not less than 10 min. after firing.

Remove the bomb from the water bath, release the pressure at a slow, uniform rate so that the pressure is reduced to atmospheric in not less than 1 min., open the bomb, and examine the inside for traces of unburned material or sooty deposits. If any are found, discard the determination, and thoroughly wash all parts of the bomb interior before using it again.

**Collection of Chlorine Solution.**—Rinse the sample crucible, the interior of the bomb, and the inner surfaces of the bomb cover with a fine jet of hot distilled water, and collect the washings in a 400-ml. beaker. Take special care not to lose any wash water.

**Determination of Chlorine.**—Acidify the bomb washings with 5 to 10 ml. nitric acid. The clear solution usually obtained can be used directly for titration. If the

ash or ferric oxide content is high enough to mask the end point of the titration, a filtering is required. Add 20 ml. of 0.025 *N* silver nitrate solution, which should be in excess, and allow it to stand for 15 min., then cool to room temperature. Add 5–10 ml. nitrobenzene, shake for 1 min., add 8 to 10 drops of the ammonium ferric-sulfate solution, and titrate the excess of silver nitrate with potassium thiocyanate solution. The end point is reached when the solution becomes faintly orange-pink in color.

### EXTRACTION OF CHLORINE BY INCINERATION WITH ESCHKA MIXTURE

The combustible matter is removed and the chlorine is retained as soluble alkali chlorides in the ignition residue by the incineration of coal sample to 775°C., in the presence of Eschka mixture and in an oxidizing atmosphere. The determination of the total chlorine is carried out titrimetrically.

**Apparatus.** Crucibles.—Porcelain or silica crucibles of 25-ml. capacity, or 50-ml. if necessary.

**Muffle Furnace.**—An electrically heated muffle furnace capable of maintaining a substantially uniform hot zone at 775°C.  $\pm$  25°C. with an air change about five times per minute.

**Silica Plate (optional).**—A silica plate of 6-mm. thickness to fit inside the muffle.

**Reagents.**—The reagents are the same as those listed for the Bomb-Combustion method, with the exception of the ammonium carbonate solution and oxygen.

**Procedure.**—Before commencing the determination, mix the sample thoroughly for at least 1 min., preferably by mechanical means.

Weigh accurately about 1 g. air-dried coal, ground to pass a 60-mesh sieve, and transfer to a porcelain capsule containing 3 g. Eschka mixture; mix thoroughly, employing a small metal spatula, and cover with 2 g. Eschka mixture. Place the capsules into a cold muffle or on the silica plate, and introduce the whole thing (plate and capsules) into a cold muffle, and gradually raise the temperature to 775°C.  $\pm$  25°C. within about one hour. Maintain this maximum temperature for about 1.5 hours, and change the air about five times per minute during the entire period of incineration, and then withdraw the capsules and allow them to cool.

**Blank.**—A porcelain capsule containing 5 g. of Eschka mixture (with no sample) for blank determination shall be included in every batch. Make the blank determination following the same procedure and using the same amounts of all reagents. This assesses both the chlorine in the reagents and any contamination from the laboratory atmosphere; the latter should be quantitatively insignificant.

**Subsequent Treatment.**—Transfer the incinerated mixture, quantitatively, to a 400-ml. beaker, and first add a small quantity of hot water and then cautiously add 40 ml. nitric acid (1:1). Cover the beaker with a watch glass, swirling and stirring the contents occasionally to expediate the dissolving.

Filter the solution into a conical flask through a rapid-filtering, hardened, and acid-washed filter paper; this procedure is usually unnecessary when 1-g. samples of low-ash coal are used. Then wash the paper with a small quantity of hot water (say four lots of 5–10 ml. each). Now determine the chlorine in the filtrate by employing the same procedure as outlined for the washings of the Bomb-Combustion method (see Determination of Chlorine, p. 1204).

**NOTE.**—The chlorine may also be determined potentiometrically.

**Calculation.**—Calculate the chlorine content of the sample as follows:

$$\text{Chlorine, \% by weight} = \frac{3.5457(A - B)N}{C},$$

where  $A$  = milliliters KCNS solution used to titrate the remaining silver in the blank determination,

$B$  = milliliters KCNS solution used to titrate the remaining silver in the sample determination,

$N$  = the normality of KCNS solution, and

$C$  = grams of sample used.

**Tolerances.**—The results of duplicate determinations carried out at different times on the same sample in the same laboratory by the same operator using the same apparatus should not differ by more than 0.02% chlorine.

The means of the results of duplicate determinations carried out in different laboratories on representative samples taken from the same bulk sample after the last stage of reduction should not differ by more than 0.02% chlorine.

## METHODS FOR THE DETERMINATION OF EQUILIBRIUM MOISTURE OF COAL AT 96 TO 97% RELATIVE HUMIDITY AND 30°C.<sup>66</sup>

**Occurrence of Moisture in Coal.**—Moisture is present in any coal, in the pure coal substance and in the mineral matter associated with coal. The moisture content of a coal sample may change in either direction depending upon conditions to which the coal is subjected; it tends toward equilibrium with the water vapor pressure of the surrounding atmosphere to which coal is exposed. However, the vapor pressure of the moisture in coal does not reach the normal tension of water vapor until the amount present exceeds a certain percentage.

**Scope.**—This method of test covers the determination of equilibrium moisture of coal equal to the percentage of water determined at 105°–110°C., retained at equilibrium by the test sample after conditioning it either from a completely wetted or a certain undersaturated stage at 30°C. in an atmosphere over a saturated solution of potassium sulfate. In order to accelerate the moisture exchange of atmosphere over the coal and the pulp of potassium sulfate, two different types of conditioning vessels are recommended:

(a) Vacuum type conditioning vessel, for equilibration of coal at absolute pressure equivalent to about 30 mm. of mercury, and

(b) Airtight conditioning vessel for use at atmospheric pressure, provided with a fan for maintaining air circulation.

In general, the results obtained by the two procedures do check reasonably well within acceptable limits.

<sup>66</sup> For further information concerning the experimental work on which these methods are based see: Krumin, P. O.: The Meigs Creek No. 9 Coal Bed in Ohio, Part III—Further Study of the Chemical and Physical Properties, and Washability Characteristics, with a Brief Review of New Methods Employed, Bulletin No. 165, Ohio State University, Engineering Experiment Station, pp. 33–38, July, 1957; Two Methods for the Equilibration of Coal over Saturated Solution of Potassium Sulfate at 30°C. (96 to 97 Per Cent Relative Humidity), (Paper presented to Meet. Amer. Group ISO/TC 27, Sub. XXVII of the ASTM D-5, May 29, 1961); R. L., Ohio State University Eng. Expt. Station, 41 pp. 1961; and The Determination of Forms of Moisture in Coal, Bulletin No. 195, Ohio State University, Engineering Experiment Station (1963).



Both methods may be used for the determination of the surface or extraneous moisture of wet coal, such moisture being the difference between total moisture as determined by standard methods,<sup>67</sup> and the equilibrium moisture.

**Significance.**—Early investigators viewed the test for equilibrium moisture as a means of determining a parameter for the classification of coal by rank only. As coal technology has advanced, the knowledge of determining the surface moisture, and that form of moisture in coal which is capillary held and does not exhibit normal vapor pressure frequently referred to as “inherent moisture,” “true bed moisture,” “moisture-holding capacity,” “capacity moisture” or “equilibrium moisture” at approximately 100% relative humidity has been generally recognized to be of practical as well as fundamental value.

For example, behavior of coal under various conditions in its preparation, transportation by conventional means or by pipelines, dewatering, drying, its alteration during storage, and various phases of industrial utilization are affected by surface and inherent moisture content.

**NOTE.**—Since there are insuperable experimental difficulties in working with atmosphere at approximately 100% relative humidity, the moisture content retained by a completely wetted coal at equilibrium in an atmosphere over a saturated solution of potassium sulfate at 30°C. (96 to 97% relative humidity) is considered equivalent to the inherent or bed moisture for Classification of Coals by Rank (ASTM Designation D388, p. 1256). It is necessary to keep in mind that the equilibrium moisture of coal is an arbitrary quantity which is affected by the size-consist of the test sample, the temperature and relative humidity of ambient air, and whether the equilibrium is reached from the completely wetted stage or from a certain under-saturated stage. In order to avoid the irreversible effect of hysteresis (especially with low rank coals) the general preference is to use, for equilibration, completely wetted coal samples, if the results are to be used for classification of coal by rank.

**Apparatus for Equilibration of Coal at Reduced Pressure.**<sup>68</sup> **Conditioning Vessel.**—A reduced pressure vessel provided with a mercury vacuum manometer and a glass or incorrodible metal stand to carry dishes loaded with coal above the level of the potassium sulfate pulp employed for maintaining relative humidity of 96 to 97% at 30°C. The stand shall be made in an arrangement which protects the dishes from spray due to frothing.

The volume of free space in the conditioning vessel is not critical but should be kept to a minimum by choice of a suitable design of vessel or by increasing the volume of pulp material.

The vessel shall be weighted to overcome its buoyancy when immersed in water.

**Weighing Bottles,** glass, low form, flat bottom, approximately 50 mm. in diameter, with inter-joint cap type standard taper 55/12 stoppers, or

**Petri-Dishes,** or incorrodible metal dishes without covers, approximately 15 mm. deep and 50 to 70 mm. in diameter, for holding the test samples during equilibration (see Note).

**Mechanical Vacuum Pump.**

**Water Bath or Insulated Air Cabinet.**—The bath or cabinet should be of sufficient size to accommodate several vacuum-type conditioning vessels, and should be provided with temperature regulator to maintain automatically a uniform temperature of  $30^{\circ} \pm 0.1^{\circ}\text{C}$ .

<sup>67</sup> ASTM Designation: D271-58, p. 1150.

<sup>68</sup> ASTM Designation: D1412-56T, Tentative Method of Test for Equilibrium Moisture of Coal at 96 to 97 Per Cent Relative Humidity and 30°C. ISO/TC Document No. 461 (Revised U.K. Method, ISO/TC 27, Document 377), August, 1959,

$$\text{Chlorine, \% by weight} = \frac{3.5457(A - B)N}{C},$$

where  $A$  = milliliters KCNS solution used to titrate the remaining silver in the blank determination,

$B$  = milliliters KCNS solution used to titrate the remaining silver in the sample determination,

$N$  = the normality of KCNS solution, and

$C$  = grams of sample used.

**Tolerances.**—The results of duplicate determinations carried out at different times on the same sample in the same laboratory by the same operator using the same apparatus should not differ by more than 0.02% chlorine.

The means of the results of duplicate determinations carried out in different laboratories on representative samples taken from the same bulk sample after the last stage of reduction should not differ by more than 0.02% chlorine.

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**Scope.**—This method of test covers the determination of equilibrium moisture of coal equal to the percentage of water determined at 105°–110°C., retained at equilibrium by the test sample after conditioning it either from a completely wetted or a certain undersaturated stage at 30°C. in an atmosphere over a saturated solution of potassium sulfate. In order to accelerate the moisture exchange of atmosphere over the coal and the pulp of potassium sulfate, two different types of conditioning vessels are recommended:

(a) Vacuum type conditioning vessel, for equilibration of coal at absolute pressure equivalent to about 30 mm. of mercury, and

(b) Airtight conditioning vessel for use at atmospheric pressure, provided with a fan for maintaining air circulation.

In general, the results obtained by the two procedures do check reasonably well within acceptable limits.

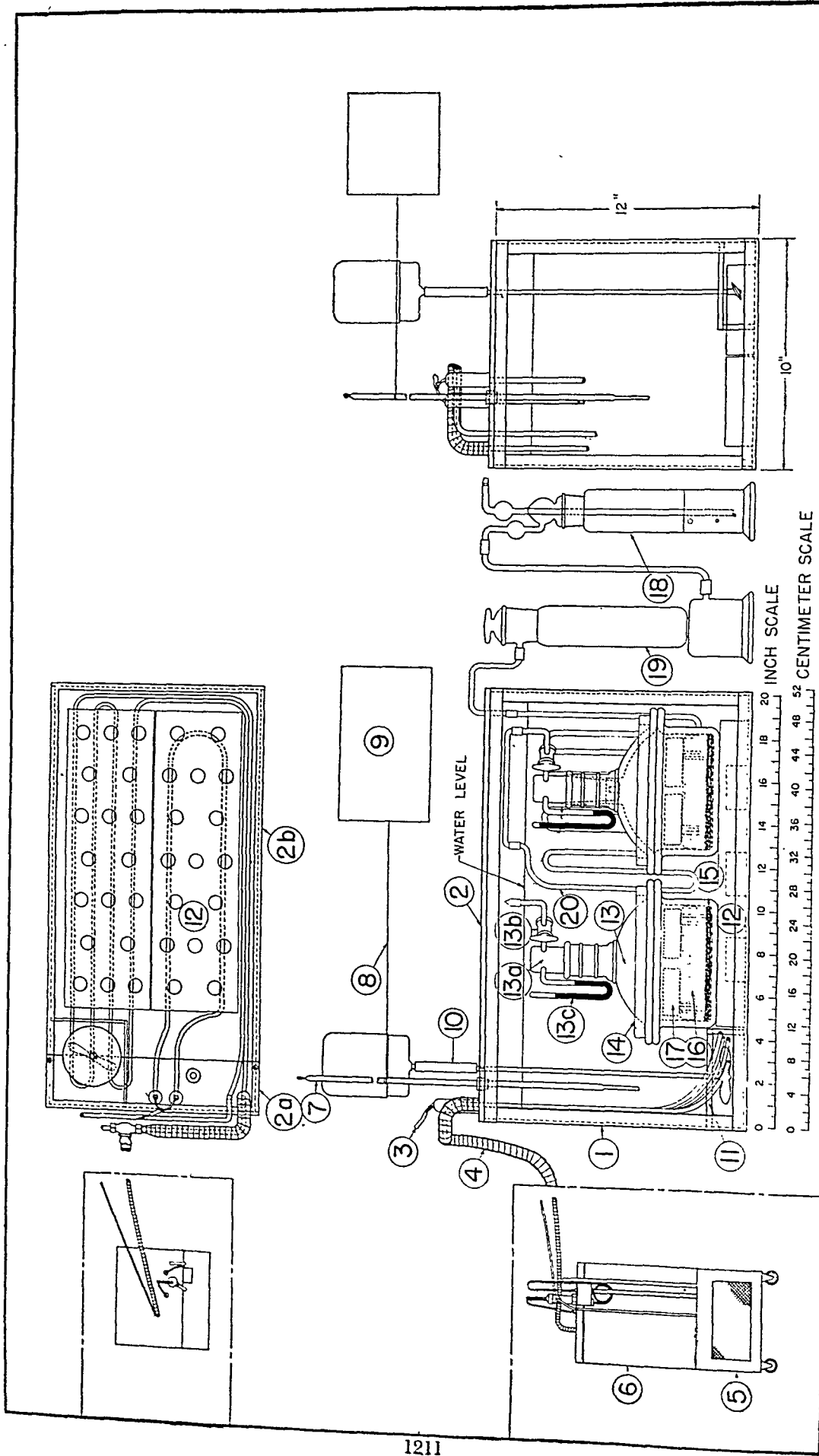


FIG. 31-16. Apparatus for the Equilibration of Coal at Reduced Pressure.

(14) *Lead ring* with which the conditioning vessel is weighted to overcome buoyancy when immersed in water.

(15) *Pulp of potassium sulfate crystals and water.*

(16) *Incorrodible metal stand* to support the sample dishes above the level of the potassium sulfate pulp, consisting of three plates; for better circulation of air and vapor the plates are spaced and each provided with three circular rows of holes; the plates are rigidly assembled in an arrangement which protects the dishes from spray due to frothing; for the same reason a rubber ring is placed around the stand.

(17) *Glass or incorrodible metal dishes* used to hold the coal samples during equilibration.

(18) *Gas washing bottle* charged with sulfuric acid (sp. gr. 1.84).

(19) *Drying jar* packed with anhydrous magnesium perchlorate, of approximately No. 8 (4380-micron) to No. 45 (350-micron) mesh size.

(20) *Spiral of copper tubing.*

**NOTE**—The thermometer (7) is provided with a metal band fastened to it at the control temperature of 30°C. and connected with the relay by means of a wire. Since the bore of the thermometer is a very fine capillary tube a small change in bath temperature causes a relatively large rise or fall of mercury. The continual rising and falling of the mercury causes the capacity of the metal band and mercury column to change, causing the relay to turn the heating element on and off.

**Special Reagent.** Potassium Sulfate ( $K_2SO_4$ ), crystals. Mix potassium sulfate crystals with water and charge into reduced pressure vessel. When the vessel is charged for the first time it should be re-evacuated several times until frothing ceases. To minimize frothing, the vessel should normally be kept evacuated.

**Sample.**—For the purpose of classification of a deposit or seam, the coal should be in fresh unchanged state. Therefore, samples shall not be taken from outcrop, weathered, or oxidized coal. Mine samples and Tipple or Shipment Samples shall be collected and prepared in accordance with the Methods of Sampling Coals (ASTM Designation: D492-48, p. 1137). If only the equilibrium moisture is desired, the commercial sampling procedure shall be used. If the surface moisture of wet coal is to be determined, the procedure for a special moisture sample shall be used.

**Preparation of Laboratory Samples.**—The samples shall be rapidly stage crushed to pass a No. 16 (1190-micron) sieve by means of a coffee-mill type crusher. The stage crushing produces a minimum amount of fine material; however, it increases segregation so the crushed sample shall be thoroughly mixed. Coals which are too wet to crush shall be spread in a thin layer and exposed to the air of the laboratory to be partly dried. Care shall be taken that low-rank coals are not overdried.

If the crushed sample cannot be examined immediately, it should be protected against oxidation and excessive drying. Storage of samples under water may be employed (see Notes).

**Procedure.**—Place 20 to 25 g. of the crushed and thoroughly mixed coal into a 250-ml. Erlenmeyer flask and add 100 ml. of recently boiled, cooled distilled water. Shake the flask mechanically for 30 minutes, and then place it in the constant-temperature bath (maintained at 30°C.) for 3 hours (see Notes). At the end of the wetting period remove the excess water from the coal by filtering on a Buechner-type funnel, approximately 65 mm. in diameter, using suction supplied by a water filter pump. Wash the filtered coal with two separate portions of

25 ml. of distilled water. In order to remove most of the adherent moisture and to prevent drying of the sample, close the funnel with a rubber stopper fitted with a glass tube, and pass air saturated with water vapor through the coal layer for ten minutes.

This treatment fully saturates the coal with water and removes interfering hygroscopic salts.

NOTES.—Mine samples and certain coals which deteriorate when treated with water may be equilibrated directly without wetting, provided the samples are collected and prepared with a minimum loss of moisture. Unwetted coals should be equilibrated for varying periods of time, in units of 24 hr., in order that equilibrium may be attained.

Employing coal samples stored under water, the wetting of samples in Erlenmeyer flasks, shaking, and placing them in constant temperature bath for 3 hours is superfluous and should be omitted.

**Equilibration.**—After draining the coal, mix thoroughly the wet coal with a spatula to correct segregation and spread approximately 2 to 5 g. of the coal in a uniform layer in a weighing bottle of known weight and with such a bottom area that the weight of dry coal per 10 sq. cm. does not exceed 1 g.

If the determination of moisture content of the analysis sample is required, quickly close the weighing bottle, and weigh to the nearest 0.2 mg. Then uncover the weighing bottle and place on the stand over the pulp of  $K_2SO_4$  in the conditioning vessel.

If only the equilibrium moisture of the sample is required, Petri-type dishes of unknown weight may be used to hold the test samples during equilibration.

Replace the cover of loaded conditioning vessel, make it gas-tight by careful grinding, greasing, and tightening of all connections. Then evacuate the vessel to an absolute pressure equivalent to about 15 to 20 mm. of mercury by means of mechanical vacuum pump, and immerse it in a constant temperature water bath (or place in an insulated air cabinet) maintained at  $30^\circ \pm 0.1^\circ C$ .

The pressure should rise quickly to about 30 mm. which is the water vapor pressure of the saturated solution of potassium sulfate at  $30^\circ C$ .

If the pressure rises above 30 mm. re-evacuate the vessel without otherwise disturbing it.

Leave the samples undisturbed in the evacuated vessel at  $30^\circ \pm 0.1^\circ C$ . and 30-mm. pressure for a period of 48 hours for all coals higher in rank than lignite; lignite will require 72 hours to reach equilibrium.

At the end of equilibration period, with the vessels still in the bath, restore the pressure in the vessel to atmospheric by slowly admitting dry air at  $30^\circ C$ . through a train consisting of:

(1) A convenient vessel (bubbler) charged with  $H_2SO_4$  (sp. gr. 1.84) and suitable for use as a flowmeter for estimating the rate of flow of air through the sulfuric acid, (18, Fig. 31-16),

(2) A drying jar charged with dry magnesium perchlorate, (19, Fig. 31-16), and

(3) A coiled copper tube placed in the constant temperature bath and connected to the inlet of the conditioning vessel, (20, Fig. 31-16).

In order to avoid changes in the moisture content there must be no disturbance of the local atmosphere immediately adjacent to the conditioned coal. It may be achieved by regulating the air inlet so that the time taken to restore atmospheric pressure in the conditioning vessel is approximately one minute for each 50 to 100 ml. of free space. (See Note.)

NOTE.—The air flow may be regulated by careful opening of the stopcock (13b, Fig. 31-16) in the cover of the conditioning vessel according to bubble count passing the  $\text{H}_2\text{SO}_4$  vessel (18, Fig. 31-16), or by including in the train a capillary tube with one end drawn out to a tip having a suitable bore for regulating the rate of air flow.

**Subsequent Treatment.**—Remove the conditioning vessel from the bath and open immediately. If a dish similar to Petri-dish is used to hold the test sample during equilibration, pour the equilibrated coal as fast as possible into a previously dried weighing bottle of known weight, quickly close it and weigh the covered bottle and its contents to determine the weight of equilibrated coal taken.

If a weighing bottle of known weight was used to hold the coal during equilibration, quickly cover the weighing bottle with its lid, wipe off with a chamois or chemically clean, lint-free cloth, allow to stand for 30 minutes in the desiccator cabinet, and weigh to the nearest 0.2 mg.

Uncover the weighing bottle with the conditioned coal, place it in the drying oven preheated to  $105^\circ\text{C}$ . and dry (lower rank coals in an atmosphere of nitrogen) at a temperature of  $105^\circ$  to  $110^\circ\text{C}$ . until constant weight (1.5 to 3 hours is normally sufficient). Then remove the weighing bottle from the oven, cover quickly, cool 30 minutes in a desiccator over  $\text{H}_2\text{SO}_4$  (sp. gr. 1.84) or calcium chloride and weigh.

**Apparatus for Equilibration of Coal at Atmospheric Pressure.** A double-walled airtight conditioning vessel provided with accessories capable of maintaining constant temperature of  $30^\circ \pm 0.1^\circ\text{C}$ . inside the vessel and a proper air circulation over the relatively large surface of wet potassium sulfate charged on the bottom of the vessel, and the surface of coal charged in conical flasks placed on a stand above the level of the pulp of potassium sulfate crystals and water.

A circulating system, thermostatically controlled, designed for circulating water of controlled temperature through the walls and, if required, other parts of conditioning vessel, capable of maintaining a constant temperature of  $30^\circ \pm 0.1^\circ\text{C}$ . inside the conditioning vessel.

Conical flasks, or weighing bottles, 50 to 70 mm. in diameter, with inter-joint, cap-type stoppers, to hold the coal samples during equilibration.

The apparatus shown in Fig. 31-17, made by P. O. Krumin and K. Svanks at The Ohio State University Engineering Experiment Station essentially according to ISO/TC 27 (Germany-13) Document No. 409, May, 1958, has been found satisfactory for equilibration of coal at atmospheric pressure.

NOTE.—Various items of equipment, such as weighing bottles, drying oven, crusher, sieve and shaking machine may be used as specified under Apparatus (p. 1209).

The apparatus (Fig. 31-17) for the equilibration of coal in airtight vessels at atmospheric pressure, consists of:

(1) A constant temperature circulating system, designed for circulating a liquid of controlled temperature through various parts of a conditioning vessel, and capable of maintaining a constant temperature of  $30^\circ \pm 0.1^\circ\text{C}$ . inside conditioning vessel.

(2) Adapter for distribution of constant temperature water for circulation through various parts of conditioning vessel.

(3) Adapter for collecting the circulating water from four outlet tubings of conditioning vessel.

(4) Mercurial thermometer ranging from 18.3° to 35°C. (65° to 95°F.), graduated in units of 0.05°F.

(5) Double-walled conditioning vessel made of copper sheet, provided with inlet and outlet tubings connected to circulating system, and a rubber gasket.

(6) Two-piece, double-walled lid, each piece provided with inlet and outlet tubings connected with adapters of the circulating system and clamps.

(7) Fan housing with shaft bearing, surrounded by a copper coil connected to adapters of circulating system, and six air intake tubes.

(8) Electric motor, designed for continuous duty with adjustment of speed, mounted in a manner that eliminates vibration.

(9) Suitable isolation sheet covering entire surface of conditioning vessel.

NOTE.—A 6- to 7-mm. thick cork isolation sheet has been found satisfactory.

(10) Mercurial thermometer ranging from 18.3° to 35°C. (65° to 95°F.), graduated in units of 0.05°F.

(11) Pulp of potassium sulfate crystals and water.

(12) Incorrodible metal disc (soldered to lower end of fan housing unit) to support the sample dishes above level of pulp.

(13) Glass tubings with flexible rubber connections to air intake tubings of fan housing chamber (7).

(14) Conical flasks used to hold samples during equilibration, or weighing bottles (not shown in the diagram).

(15) Fan (mounted on metal rod provided with roller bearing and connected with motor shaft) to accelerate moisture exchange by circulating air from sample dishes, over wet potassium sulfate and back.

(16) Inlet and outlet tubings for purging the vessel with nitrogen (not shown in the diagram).

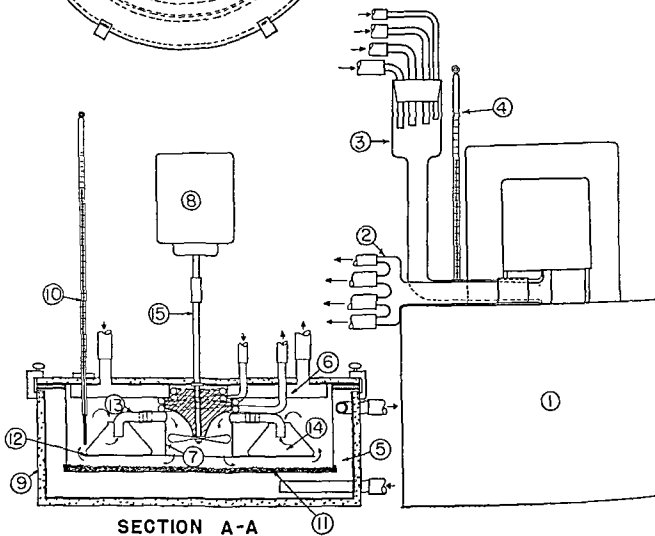
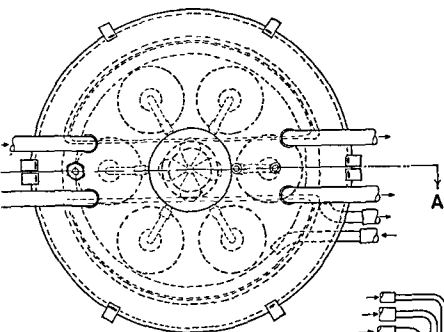
**Special Reagent. Potassium Sulfate ( $K_2SO_4$ ) Crystals.**—Mix potassium sulfate crystals with water and charge into atmospheric pressure vessel.

**Procedure.**—Place 2 to 5 g. of thoroughly mixed coal (previously treated according to the procedure described on p. 1212) into a conical flask (14, Fig. 31-17) and spread evenly over the bottom of the flask. Place the flask on the stand (12, Fig. 31-17) of the conditioning vessel which is kept at a temperature of  $30^\circ \pm 0.1^\circ\text{C}$ . Put the air suction tube (13) in the conical flask, close the vessel, make it airtight by applying rubber gasket and clamps, and switch on the fan for maintaining air circulation.

The time of conditioning depends on rank of the coal and the quantity of moisture to be exchanged. Several determinations should be made using varying conditioning periods from 4 to 24 hours or more in units of 4 hours. The results will indicate whether equilibrium has been attained in the shorter period.

NOTE.—According to ISO Document No. 622, submitted by the German delegation, the equilibrium could be reached in a period of 2–4 hours, if the excess moisture of the test sample, after filtering on a Buechner-type funnel, is further reduced by pressing the sample between layers of absorbent paper.

At the end of conditioning period lift the lid of the vessel, remove the air suction tube, and pour the conditioned coal as fast as possible from the conical flask into



SECTION A-A

0 3 6 9 12 15 INCH SCALE

0 4 8 12 16 20 24 28 32 36 40 CENTIMETER SCALE



a weighing bottle which has been previously heated with its lid at 105°–110°C., cooled in a desiccator and weighed with its lid. Quickly close the weighing bottle, and weigh the covered bottle with its contents to determine the weight of equilibrated coal sample taken. Uncover the weighing bottle with the conditioned coal, place in a preheated drying oven (at 105°–110°C.) and follow the same procedure for the determination of moisture as described in the second paragraph under Subsequent Treatment, p. 1214.

**Simultaneous Determination of Forms of Moisture.**—Simultaneous determination of total, surface, and equilibrium moisture may be conveniently made employing equilibration procedure either at reduced or at atmospheric pressure. For this purpose, the test sample must be placed into a weighing bottle of known weight (Petri dish or conical flask without lid cannot be used) and weighed before equilibration, in order to establish the weight of the sample taken. Weighing of the test sample with weighing bottle plus lid before equilibration is the only additional step required for simultaneous determination of the three forms of moisture under consideration. All other steps of the procedure shall be carried out as described before for the determination of equilibrium moisture.

**NOTE.**—For additional information regarding the experimental work on which simultaneous determination of forms of moisture is based, see P. O. Krumin, *Forms of Moisture in Coal*, Bulletin No. 195, Ohio State University Engineering Experiment Station, 1963.

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FIG. 31-17. Diagram of Apparatus for the Equilibration of Coal at Atmospheric Pressure.  
See facing page.

- (1) A constant temperature circulating system, designed for circulating a liquid of controlled temperature through various parts of the conditioning vessel; the circulating system shall be capable of maintaining a constant temperature of  $30^{\circ} \pm 0.1^{\circ}\text{C}$ . inside the conditioning vessel.
- (2) Adapter for distribution of constant temperature water for circulation through various parts of conditioning vessel.
- (3) Adapter for collecting the circulating water from four outlet tubings of the conditioning vessel.
- (4) Thermometer, mercurial, covering a range from 18.3 to 35°C. (65 to 95°F.), graduated in units of 0.05°F.
- (5) A double-walled conditioning vessel made of copper sheet, provided with inlet and outlet tubings connected with the circulating system.
- (6) A two-piece double-walled lid, each piece provided with inlet and outlet tubings connected with adapters of the circulating system.
- (7) A fan housing with shaft bearing surrounded by a copper coil connected with adapters of the circulating system, and six air intake tubes.
- (8) A motor stirrer, electric, designed for continuous duty with adjustment of stirring speed.
- (9) A suitable isolation sheet covering the entire surface of the conditioning vessel.
- (10) Thermometer, mercurial, covering a range from 18.3 to 35°C. (65 to 95°F.), graduated in units of 0.05°F.
- (11) Pulp of potassium sulfate crystals and water.
- (12) Incorrodible metal disc (soldered to the lower end of the fan housing unit) to support the sample flasks above the level of the pulp.
- (13) Glass tubings with flexible rubber connections to the air intake tubings of the fan housing chamber (7).
- (14) Conical flasks used to hold the coal samples during equilibration.
- (15) A fan (mounted on metal rod connected with motor shaft) used to accelerate the moisture exchange by circulating air from the conical sample flasks over the wet potassium sulfate and back, into the sample flasks.

**Calculation.**—Calculate the percentage of moisture in the coal sample as follows:

$$\text{Total moisture} = \frac{W_2 - W_4}{W_2 - W_1} \times 100,$$

$$\text{Surface moisture} = \frac{W_2 - W_3}{W_2 - W_1} \times 100,$$

$$\text{Equilibrium moisture} = \frac{W_3 - W_4}{W_3 - W_1} \times 100,$$

where  $W_1$  = weight of empty weighing bottle plus cover (g.),

$W_2$  = weight of weighing bottle plus cover plus coal sample before equilibration (g.),

$W_3$  = weight of weighing bottle plus cover plus coal after equilibration (g.), and

$W_4$  = weight of weighing bottle plus cover plus coal sample after drying (g.)

**Report.**—Report the equilibrium moisture to the nearest 0.1% as the percentage loss in weight of the equilibrated coal.

**Precision.**—The permissible differences between two or more determinations carried out in different batches shall not exceed the following values:

<i>Equilibrium Moisture, %</i>	<i>Repeatability (The same operator, the same apparatus), %</i>	<i>Reproducibility (Different Laboratories), %</i>
under 5	0.3	0.5
5 to 15	0.5	1.0
over 15	1.0	1.5

### SAMPLING AND ANALYSIS OF COAL FOR VOLATILE MATTER DETERMINATION IN CONNECTION WITH SMOKE ORDINANCES<sup>69</sup>

This method is limited to the sampling and analysis of coal for volatile matter determination reported on the moisture- and ash-free basis in connection with smoke ordinances regarding permissible volatile matter content of solid fuels.

**Procedure.**—The content of volatile matter of a specific lot of coal shall be determined by analyzing a gross sample of not less than 90 lb., consisting of a minimum of nine increments, each increment weighing not less than 10 lb. Sampling and analysis shall be carried out as described in the following paragraphs.

**Collection of Gross Sample.**—The procedure for collecting the increments shall fulfill all of the requirements of good sampling as specified in Section 2 and Section 6 of the Standard Methods of Sampling Coals Classified According to Ash Content (ASTM Designation: D192, p. 1137).

**Reduction of Sample.**—The 90-lb. minimum gross sample obtained by the procedure prescribed in Paragraph (a) shall be reduced for analysis by mechanical preparation in accordance with Section 7 of Standard Methods D192, page 1.

<sup>69</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D980-53.

**Analysis of Sample.**—The laboratory determination for volatile matter content shall be made in accordance with Section 16 (a) and (c), Section 17 and Section 18 (b) of the Standard Methods of Laboratory Sampling and Analysis of Coal and Coke (ASTM Designation: D271, p. 1152).

Moisture and ash determinations for use in calculating volatile matter to a moisture- and ash-free basis shall be made on the laboratory sample used for the volatile matter determination. The moisture determination shall be made in accordance with Sections 9 to 11 of Standard Methods D271 (p. 1150), and the ash determination in accordance with Section 13 and Section 14 of Standard Methods D271.

**Report.**—Volatile matter shall be reported as a percentage of the moisture- and ash-free coal, and shall be calculated as follows:

$$\text{Volatile matter in moisture- and ash-free coal} = \frac{\text{Volatile matter as determined}}{100 - (\text{moisture} + \text{ash})} \times 100$$

**Reproducibility of Results.**—This method is intended for an accuracy such that if a large number of samples were taken, as described above, from an equally large number of lots of similar coal then, on the average, in 99 out of 100 cases the test values for the percentage of moisture- and ash-free volatile content would have an accuracy within plus or minus 1.0.

## GRINDABILITY OF COAL BY THE HARDGROVE-MACHINE METHOD <sup>70</sup>

**Scope.**—This method <sup>71</sup> is used to determine the relative grindability or ease of pulverizing of coals in comparison with a coal chosen as 100 grindability. The method is based on Rittinger's Law, which states: "The work done in pulverizing is proportional to the new surface produced." A prepared sample receives a definite amount of grinding energy in a miniature pulverizer, and the new surface is determined by sieving.

**Apparatus.**—The apparatus shall consist of the following:

**Grindability Machine.**—A grindability machine such as is shown in Fig. 31-18 is required for this test. The eight 1-in. balls roll on a stationary ring and are driven from above by a rotating ring. The action of the rolling balls causes an increase in the surface of the sample being tested. A definite pressure of  $64 \pm \frac{1}{2}$  lb. on the balls is obtained by the weights, shaft, top grinding ring, and gear. A predetermining counter is used to stop the motor automatically as soon as the vertical shaft of the grindability machine has made exactly 60 revolutions.

**Sieves.**—The following sieves will be required: 1190-micron (No. 16), 590-micron (No. 30), and 74-micron (No. 200). The sieves shall conform to the Specifications for Sieves for Testing Purposes (ASTM Designation: E11, p. 1277).

**Mechanical Sieving Device.**—A mechanical sieving device is desirable, although

<sup>70</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D409-51.

<sup>71</sup> For information concerning the experimental work on which this method is based, see paper by R. M. Hardgrove, Grindability of Coal, *Transactions, Am. Soc. Mechanical Engrs.*, 54, F.S.P., p. 37, 1932.

Another method of test for the grindability of coal, Method of Test for Grindability of Coal by the Ball-Mill Method (D408-37T), was published as tentative by the Society from 1937 to 1951, but was discontinued in 1951.

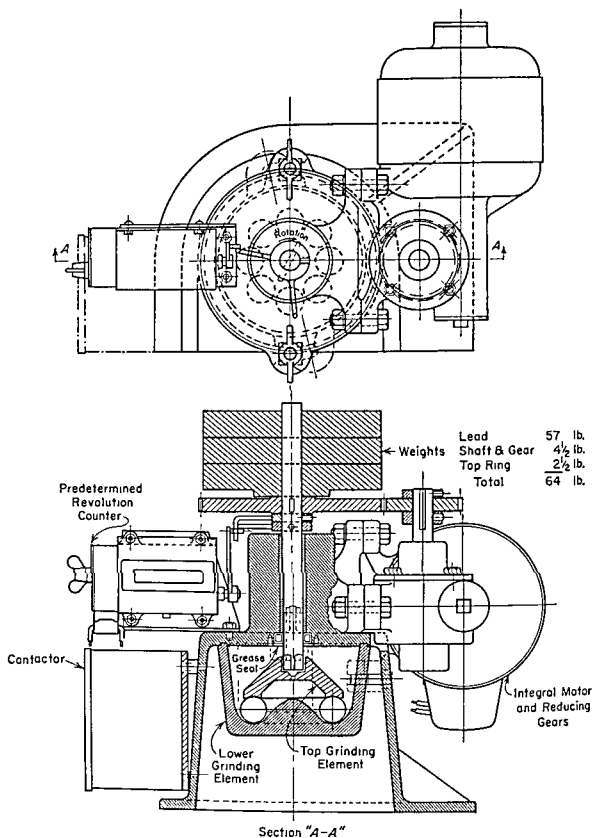


FIG. 31-18. Hardgrove Grindability Machine.

not necessary. If a mechanical sieving device is not available, it will be necessary to give the sample an equivalent amount of hand sieving.

**Balance.**—A triple beam balance having a sensitivity of 0.01 g., with which weighings from 0.01 to 111 g. can be made, is well adapted for this test. However, a torsion or trip balance with suitable pan, of the specified sensitivity, may be used. Greater sensitivity than 0.01 g. is not necessary for this test.

**Laboratory Crusher.**—The sizing of the sample to be placed in the grindability machine shall be such that it will pass the 1190-micron (No. 16) sieve, and remain on the 590-micron (No. 30) sieve. In order to break up the coarser particles of the sample being prepared for test, a laboratory crusher or a coffee mill will be found desirable. The use of such a device allows the reduction of the coarser particles without the production of excess fine material.

**Gross Sample.**—A representative gross sample of coal should be collected and prepared by crushing to pass a 4760-micron (No. 4) sieve in accordance with the Methods of Sampling Coals Classed According to Ash Content (ASTM Designation: D492, p. 1137).

**Preparation of Sample.**—An air drier and a small riffle sampler as described under the Methods of Laboratory Sampling and Analysis of Coal and Coke (ASTM Designation: D271, pp. 1145-1146), or equivalent, are desirable in preparing the sample. Place the laboratory sample, after air drying until the loss in weight is not more than 0.1% per hour, on the 1190-micron (No. 16) sieve nested with a 590-micron (No. 30) sieve and bottom pan. Shake the sieves by a mechanical sieving machine for approximately 2 min., or by an equivalent amount of hand sieving. Put the material remaining on the 1190-micron sieve into a laboratory crusher or a coffee mill in which the set screw has been adjusted so that the coarsest particles are broken up. Return the sample after passing it through the laboratory crusher or coffee mill to the 1190-micron sieve of the nest of sieves, and again shake it by the mechanical sieving machine or by hand sieving. Repeat this operation several times until the entire sample has passed through the 1190-micron sieve. Then shake the material remaining on the 590-micron sieve to thoroughly remove any material smaller than this size. Discard all material passing the 590-micron sieve. By using this method of preparing the sample, a minimum of fines is produced.

**Operation of Grindability Machine.**—Set the predetermined counter so that the machine will automatically stop after 60 revolutions have been completed. To ensure stoppage of the machine within one-quarter of one revolution, two trippers are furnished. One tripper is fixed, and the other may be set to correspond with the coasting of the machine after the switch is opened. Therefore, the number of counts on the counter will be 120, or just twice the number of revolutions made by the machine. Clean the grinding elements thoroughly by brushing them before the sample to be tested is added. Place the eight 1-in. diameter balls in the bottom of the lower grinding element and distribute 50 g. of the prepared No. 16 to No. 30 size sample evenly over the balls. Brush any material falling on the elevated section of the lower grinding element towards the balls. Then place the upper grinding element on the balls and fit the lower end of the shaft to the square opening in the disk and fasten the grinding elements securely in place by two thumb screws on the sides of the lower grinding element. Care shall be taken to pull the bowl up evenly with the thumb screws. The set screw on the collar which supports the driving gears shall always be kept tight, otherwise the weights will rest on the frame and there will be no pressure on the balls. Set the predetermining counter

to zero, and close the starting switch. After the machine has been automatically stopped, transfer the sample to the 74-micron (No. 200) sieve.

**Sieving.**—Shake the 74-micron (No. 200) sieve by a mechanical sieving machine for 10 min., or by an equivalent amount of hand sieving. Then remove the sieve and clean the underside carefully with a 1-in. bristle brush in order to remove any adherent material. Then shake the sample by the mechanical sieving machine for 5 min. more or by an equivalent amount of hand sieving, after which the brushing of the underside of the sieve shall be repeated. After an additional 5 min. of sieving, the material is ready for weighing. A total of 20 min. of mechanical sieving, or an equivalent amount of hand sieving, should result in a comparatively clean sieve.

**Weighing the Sample.**—Coals having a high residual moisture content (this is especially true of lignites) lose some of their residual moisture when in a pulverized condition. For this reason, rapid and fairly accurate weighing is essential. Discard the material passing through the 74-micron (No. 200) sieve, weigh the material retained on the sieve to within 0.1 g., and record the weight.

**Calculation.**—The grindability index shall be calculated as follows:

$$\text{Hardgrove grindability index}^{72} = 13 + 6.93W$$

where  $W$  = weight of material passing the 74-micron (No. 200) sieve, determined from the weight of the original sample (50 g) minus the weight of the material retained on the 74-micron (No. 200) sieve.

**Reproducibility of Results.**—The permissible variation between two or more determinations shall not exceed the following:

	<i>Per Cent</i>
Same laboratory.....	2
Different laboratories.....	3

### DROP SHATTER TEST FOR COAL<sup>73</sup>

This method of drop shatter test<sup>74</sup> is intended for determining the relative size stability and its complement, the friability, of sized coal. It affords a means of indicating the ability of coal to withstand breakage when subjected to handling at the mine and during transit to the consumer. The test is serviceable for ascertaining the similarity of coals in respect to size stability and friability rather than for determining values within narrow limits in order to emphasize their dissimilarity.

<sup>72</sup> The calibration of the machine may be checked by running reference samples, information about which may be had by request to Society Headquarters, 1916 Race St., Philadelphia 3, Pa.

<sup>73</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D440-49.

<sup>74</sup> For information concerning the development and utilization of this drop shatter test method for coal the following references may be consulted:

C. M. Smith, An Investigation of the Friability of Different Coals, University of Illinois, Engineering Experiment Station, Bulletin No. 196, 1929; The Friability of Illinois Coals, University of Illinois, Engineering Experiment Station, Bulletin No. 218, 1930.

H. F. Yancey and R. E. Zane, Comparison of Methods for Determining the Friability of Coal, U. S. Bureau of Mines, Report of Investigations 3215, 1933.

R. E. Gilmore, J. H. H. Nicolls and G. P. Connell, Coal Friability Tests, Canadian Department of Mines, Mines Branch, No. 762, 1935.

This method is considered applicable for testing a selected size of different coals, for testing different single sizes of the same coal, and for mixed sizes of the same or different coals (see Note).

NOTE.—By single sizes is meant those with fixed upper and lower screen opening limits, selected from those designated under Screens (next section), and by mixed sizes is meant either "slack" or a mixture of two or more single sizes.

This test appears best suited for measuring the relative resistance to breakage of the larger sizes of coal when handled in thin layers such as from loader to mine car, from loading boom to railroad car, from shovel to chute, etc. While it may not be so well adapted for measuring the liability to breakage of coal when handled in mass, as in unloading open-bottom cars, emptying bins, etc., it is believed that the method of test will serve also to indicate the relative size stability of composite sizes of coal where, in commercial handling, the smaller sized pieces have a cushioning effect which tends to lessen the breakage of the larger pieces of coal.

**Apparatus. Shatter Test Machine.**—The shatter test machine, which is the same as that described and illustrated in the Method of Drop Shatter Test for Coke (ASTM Designation: D141, p. 1268), shall consist of a box 18 in. in width, 28 in. in length, and approximately 15 in. in depth, supported above a rigidly mounted cast-iron or steel plate not less than  $\frac{1}{2}$  in. in thickness, 38 in. in width, and 48 in. in length. The inside of the bottom of the box shall be 6 ft. above the plate. The bottom of the box shall consist of two doors hinged lengthwise and latched so that they will swing open freely and not impede the fall of the coal. Boards about 8 in. in height should be placed around the plate so that no coal is lost. To prevent the breakage of coal, which may occur while placing the sample in the box, the box shall be constructed so that it can be lowered to a convenient level; this is best done by means of a pulley and counterweight. A convenient form of shatter test machine is shown in Fig 31-19.

**Screens.**—Round-hole screens selected from the following sizes, 8, 6, 4, 3, 2,  $1\frac{1}{2}$ , 1,  $\frac{3}{4}$ ,  $\frac{1}{2}$ ,  $\frac{1}{4}$ , and  $\frac{1}{8}$  in., should be used. These screens should conform to the Specifications for Sieves for Testing Purposes (ASTM Designation: E11, p. 1277). Frames for the screens may be of either hardwood or metal, and may be square, rectangular, or circular. A nest comprising all the screens in the series, with 2-ft. square plates, that is, of 4-sq. ft. area, is recommended, although plates with areas of 6 to 9 sq. ft., are suitable.

**Collection of Gross Sample.**—The gross sample should be obtained in accordance with instructions given in the Method of Test for Screen Analysis of Coal (ASTM Designation: D410, p. 1231). In order that the entire quantity of the coal sampled will be represented proportionately in the gross sample, increments should be regularly and systematically collected. When testing coal as mined, the sample should be taken at the mine before it is subjected to screening and to loading into cars at the tippie. When testing coals subsequent to mining, the sample may be taken at any stage in the transportation from the mine to the place at which it is to be used. For the correct interpretation of the shatter test results, the elapsed time since mining as well as a record of the handling and storage of the coal should be noted.

**Preparation of Laboratory Sample.**—Using the screens designated above, make a preliminary screening of a representative portion or all of the gross sample and retain the screened sizes separately. Screen successive representative portions of the gross sample to obtain at least 200 lb. of the single size selected for test. While





ing screen opening and to be retained on the lower. Place only a thin layer of coal on the screen so as to allow the pieces to be in direct contact with the screen openings. Individual pieces of coal not passing readily through either of the screens shall be tried by hand to determine whether they will pass through the openings in any position without forcing.

For slack coals and mixed sizes, carefully prepare the sample either by the process of quartering or by reassembling the different sizes in the proportion obtained in the preliminary screening of the lot of coal to be tested. For slack coals in which the largest pieces will not be retained on a screen with  $\frac{3}{4}$ -in. openings, quartering is satisfactory; while for larger sized slack coals and for blends of two or more single sizes, the reassembling method is recommended. Before dropping, screen the samples prepared by quartering on the same set of screens selected for the dropped coal.

**Procedure.**—A 50-lb. portion of the coal sample, prepared in accordance with the preceding section, shall be given two drops. Place the coal in the box of the shatter test machine, level it, and then drop it a distance of 6 ft. onto the plate. Carefully return all the coal on the plate to the box and again drop it. After the second drop, separate the material into sized portions using the screens specified above. In screening, care shall be taken to prevent further breakage of the coal. The screening shall be carried out in such small increments as to permit satisfactory contact between the individual pieces of coal and the screen. On the larger screens, down to and including the screen with 1-in. openings individual pieces of coal not readily passing through the screens shall be tried by hand to determine whether they will pass through the openings in any position without forcing. When using the screens with  $\frac{3}{4}$ -in. openings and smaller, the coal shall come into intimate contact with the screen either by shaking or rolling by hand without upending the individual pieces.

Weigh the coal remaining on each screen, and that which passes through the bottom screen either separately or in a cumulative manner on a scale sensitive to  $\frac{1}{4}$  lb. or less. By the cumulative method, weigh the largest pieces into a tared container and add each successive smaller size to this. Weigh the total amount after each addition. If the final net weight so obtained shows a loss of over 1%, reject the test and make another. In each case where the loss is less than 1%, it shall be considered as material passing the  $\frac{1}{2}$  in. or other bottom screen used, and shall be included with this size. Make at least two tests to obtain size stability results agreeing within 2%. When three or more tests are considered advisable and are made, all the results within a maximum to minimum limit of 3% may be averaged.

**Report.**—(a) The percentage weight screen analysis shall be reported to the nearest 0.1 per cent, and the percentage size stability to the nearest 0.5 per cent.

(b) Numerical examples of tabulating the results and of calculating the size stability in per cent and the friability in per cent are shown in Tables 31-5 and 31-6. The form shown in Table 31-5 is general and serviceable for both single and mixed sizes. The form in Table 31-6, in which the example shown is for a 4- to 6-in. size, is serviceable for other single sizes. The screen with  $\frac{1}{2}$ -in. openings is suggested as the bottom screen for testing single sizes, 2 to 3 in. and larger. For smaller single sizes, slack coals, and mixed sizes containing slack, two additional (bottom) screens, with  $\frac{1}{4}$ - and  $\frac{1}{8}$ -in. openings, are recommended.

TABLE 31-5. GENERAL FORM FOR REPORTING DATA AND CALCULATIONS

Round-Hole Screens, in.		Weight, %		Average of Screen Size Openings, in.	Product of Weight Percentage and of Screen Openings	
Retained on	Passing	Before Test	After Test		Before Test	After Test
8						
6	8	...	...	7.000	...	...
4	6	...	...	5.000	...	...
3	4	...	...	3.500	...	...
2	3	...	...	2.500	...	...
1½	2	...	...	1.750	...	...
1	1½	...	...	1.250	...	...
¾	1	...	...	0.875	...	...
½	¾	...	...	0.625	...	...
¼	½	...	...	0.375	...	...
⅛	¼	...	...	0.185	...	...
	⅛	...	...	0.060	...	...
Total passing ¾		...	...	0.185	...	...
Total passing ¼		...	...	0.125	...	...
Average size of coal before and after test (two drops), in. . .					Total, S ...	Total, s ...

$$\text{Size stability, \%} = \frac{100 \times s}{S} = \dots\dots\dots$$

$$(\text{Friability, \%} = 100 - \text{size stability})$$

### TUMBLER TEST FOR COAL <sup>75</sup>

This tumbler test <sup>76</sup> is intended for determining the relative friability of a particular size of sized coal. It affords a means of measuring the liability of coal to break into smaller pieces when subjected to repeated handling at the mine or

<sup>75</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D441-45.

<sup>76</sup> For information concerning the development and utilization of this tumbler test method for coal, the following references may be consulted: J. H. H. Nicolls, Friability Tests on Various Fuels Sold in Canada, Paper II, Canadian Department of Mines, Mines Branch, No. 644, 1926; I. Lavine, A. W. Gauger, and C. A. Mann, Studies in the Develop-

TABLE 31-6. FORM AND EXAMPLE FOR REPORTING DATA AND CALCULATIONS FOR A SELECTED SINGLE SIZE

Round-Hole Screens, in.		Weight Record- ed, lb.	Weight, per cent (1)	Average of Screen Openings		Product of (1) × (3)
Retained on	Passing			Inches (2)	Factor (3)	
SAMPLE						
4	6	50	100.0	5.000	1	100.00 = <i>S</i>
DROPPED COAL						
4	6	24½	48.5	5.000	1	48.500
3	4	7	15.0	3.500	0.7	10.500
2	3	6½	13.0	2.500	0.5	6.500
1½	2	3	6.0	1.750	0.35	2.100
1	1½	2½	5.0	1.250	0.25	1.250
¾	1	1½	3.0	0.875	0.175	0.525
½	¾	1½	3.0	0.625	0.125	0.375
	½	¾	6.5	0.250	0.05	0.325
Total (Sum of products (1) × (3) for dropped coal) . . . . .						70.075 = <i>s</i>

$$\text{Size stability, \%} = \frac{100 \times s}{S} = \frac{100 \times s}{100} = s = 70.1$$

To be reported as: Size Stability, 70%

$$(\text{Friability, \%} = 100 - 70 = 30)$$

subsequently, by the distributor or by the consumer. The test is serviceable for ascertaining the similarity of coals in respect to friability rather than for determining values within narrow limits in order to emphasize their dissimilarity. This

ment of Dakota Lignite, Industrial and Engineering Chemistry, 22, No. 12, p. 1360, 1930; C. E. Lawall and C. T. Holland, Some Physical Characteristics of West Virginia Coals, Am. Inst. Mining and Metallurgical Engrs., Coal Division, 101, p. 100, 1930; H. F. Yancey, K. A. Johnson, and W. A. Selvig, Friability, Slacking Characteristics, Low Temperature Carbonization Assay and Agglutinating Value of Washington and Other Coals, U. S. Bureau of Mines Technical Paper No. 512, 1932; H. F. Yancey and R. E. Zane, Comparison of Methods for Determining the Friability of Coal, U. S. Bureau of Mines, Report of Investigations 3215, 1933; and R. E. Gilmore, J. H. H. Nicolls, and G. P. Connell, Coal Friability Tests, Canadian Department of Mines, Mines Branch No. 762, 1935.

method also may serve to indicate the relative extent to which sized coals will suffer size degradation in certain mechanical feed devices. The test may be employed for differentiating between certain ranks and grades of coal, and therefore the method is of service for coal classification purposes.

**Apparatus. Porcelain Jar Tumbler.**—The tumbler should consist of a cylindrical porcelain jar of uniform dimensions,  $7\frac{1}{4}$  in. in diameter and  $7\frac{1}{4}$  in. in depth, inside measurements, such as is employed for pulverizing coal samples for analysis.

The jar should be fitted inside with an iron frame with lifting shelves constructed as shown in Fig. 31-20. The two rings, *a*, should be  $7\frac{1}{8}$  in. in outside diameter and should be made of  $\frac{3}{4}$ - by  $\frac{1}{8}$ -in. iron. The three ledges or shelves, *b*,  $6\frac{1}{2}$  by  $\frac{3}{4}$  by  $\frac{1}{8}$  in., should be attached radially to the rings by means of small brackets, *c*, the ends of the shelves being flush with the outer edges of the rings. The shelves should be attached so that there will be  $\frac{5}{16}$ -in. clearance between their outer edge and the outside of the ring. Rivets, not bolts, should be used in constructing the frame. As the jars available commercially are not of absolutely uniform size, the measurements of the frame may be slightly varied to suit individual cases. The frame should be fixed inside the jar by means of wedges between the rings and the inside wall of the jar so that its axis shall coincide as nearly as possible with the axis of the jar, and so that the frame will rotate with the jar. The jar should be closed by a set-in porcelain lid resting upon a heavy rubber gasket and sealed tightly according to the customary procedure with such jars, that is, by means of a bolt working against the lid. The bolt should be set in a crossbar, the ends of which should be held by a metal strip which fits around the body of the jar. For tumbling, the jar should be laid in a

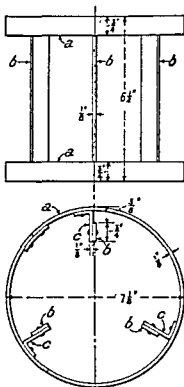


FIG. 31-20. Steel Frame  
Used in Jar Mill.

horizontal position in a suitable support or rack and rotated about its cylindrical axis at the rate of 40 r.p.m.

**Optional Iron Jar Tumbler.**—An iron jar may be substituted for the porcelain jar specified in the preceding paragraph, provided it has approximately the same internal dimensions, namely,  $7\frac{1}{4}$  in. in diameter by  $7\frac{1}{4}$  in. in depth. A jar constructed of cast iron is recommended, the interior of which should be machined to the required internal dimensions. For making it sufficiently light for lifting, the jar may have a wall thickness of not less than  $\frac{1}{4}$  in., except at each end. It is recommended that the lid, the rubber gasket, and the metal strip which passes from the bottom up the outside of the jar to serve in holding in place the crossbar above the lid, be similar in design with those for the porcelain jar. The wall of the iron jar for a distance of approximately 1 in. from the top should have a thickness of at least  $\frac{1}{2}$  in. to correspond with that of the porcelain jar; and in order that the metal strip may fit evenly, the lower inch of the wall should also have a thickness of not less than  $\frac{1}{2}$  in.

**Sieves.**—For sizing the sample for test, square-hole sieves having 1.50- and 1.06-in. actual openings between the wires should be used. These sieves may be fitted into

frames, 12 by 30 in. or larger. For screening the coal after tumbling, square-hole sieves having 1.06, 0.750, 0.530, 0.375, 0.0469, and 0.0117-in. actual openings between the wires shall be used. For this purpose, round, metal-framed screens 8 in. in diameter are suitable. The sieves should conform to the Specifications for Sieves for Testing Purposes (ASTM Designation: E11, p. 1277).

**Balance.**—The balance used for weighing the sample should be sensitive to 1 g.

**Collection of Gross Sample.**—The gross sample of coal should be obtained in accordance with Sections 1 to 4, inclusive, and Section 6 of the Methods of Sampling Coals Classed According to Ash Content (ASTM Designation: D492, p. 1137).

**Preparation of Sample.**—Make a preliminary sieving of a representative portion, approximately 100 lb., of the gross sample, using square-hole sieves with 1.06- and 1.50-in. openings. If this preliminary sieving indicates that the pieces of coal are mostly smaller than 1.50 in., sieve successive representative portions of the gross sample until at least 25 lb. of the 1.06- to 1.50-in. size are obtained. If most of the pieces obtained by the preliminary sieving are larger than 1.50 in., conduct sieving of representative portions of the gross sample until at least 50 lb. of the sieved material remaining on the 1.06-in. sieve are available. Then break the pieces so obtained that are larger than 1.50 in. with a hammer until they pass the 1.50-in. sieve, avoiding as much as possible the production of pieces smaller than 1.06 in. Should the combined weights of the 1.06- to 1.50-in. size, obtained by sieving before and after hammer breakage of the larger pieces, be less than the required 25 lb., augment the amount by further sieving and breakage of additional representative portions, or the remainder of the gross sample, care being taken to discard all pieces in which noticeable cracks have developed by hammer breakage. Care should also be taken to provide pieces covering the whole range of the 1.06- to 1.50-in. size in both the 25-lb. composite sample, and in each 1000-g. sample taken for test as in the following section. This may be accomplished by the use of a 1.25-in. sieve to see that approximately half of the weight of the pieces comprising these samples will be between 1.06 and 1.25 in. and half between 1.25 and 1.50 in.

Mix thoroughly the total quantity of the 1.06- to 1.50-in. size and then resieve it to pass the 1.50-in. sieve and be retained on the 1.06-in. sieve. Place only a thin layer of coal on the sieve so as to allow the pieces to be in direct contact with the sieve openings. Upend by hand individual pieces of coal not passing readily through the sieve to determine whether in any position they pass the sieve.

**Procedure.**—Weigh approximately 1000 g. of the coal sample prepared in accordance with the preceding section and place it in the jar. Rotate the jar for 1 hr. in the tumbler test machine at  $40 \pm 1$  r.p.m. In order to standardize the time of tumbling, a revolution counter should be used, either periodically or as permanent accessory equipment to the machine, to ensure that the total number of revolutions during a test is approximately 2400. After tumbling, thoroughly grade the coal as to size upon the sieves designated on p. 1228. Carry out the sieving in such small increments as to permit satisfactory contact between the individual pieces of coal and the sieve. On the two larger sieves, 1.06- and 0.750-in., upend by hand individual pieces of coal not readily passing through the sieves to determine whether in any position they pass the sieve.

Sieving may be carried out either by hand or mechanically, though the former method is preferable.

Make at least four single-jar tests, and, provided sufficient sample is available, it

TABLE 31-7. SIEVE ANALYSIS OF COAL USING SQUARE-HOLE SIEVES

Retained on	Passing	Weight, % (1)	Average of Sieve Openings		Product of (1) × (3)
			Inches (2)	Factor (3)	
SAMPLE					
1.06 in.	1.50 in.....	100.0	1.280	1	100.00 = S
TUMBLER COAL					
1.06 in.	1.50 in.....	46.2	1.280	1	46.2
0.750 in.	1.06 in.....	26.9	0.905	0.7	18.83
0.530 in.	0.750 in.....	4.0	0.640	0.5	2.00
0.375 in.	0.530 in.....	1.6	0.452	0.35	0.56
0.0469 in.	0.375 in.....	5.5	0.211	0.16	0.880
0.0117 in.	0.0469 in. (No. 16).....	0.5	0.029	0.023	0.012
	0.0117 in. (No. 50) <sup>a</sup> .....	15.3 <sup>b</sup>	0.006	0.005	0.077
Total (Sum of products (1) × (3) for tumbled coal).....					68.56 = s

$$\text{Friability, \%} = \frac{100(S - s)}{S} = \frac{100(100 - 68.56)}{100} = 31.4$$

To be reported as: Friability, 31.5 per cent

<sup>a</sup> Including loss, not to exceed 0.5 per cent.

<sup>b</sup> The percentage of "fines and dust" passing the 0.0117-in. (No. 50) sieve represents the proportion of the breakage due to attrition or abrasion rather than to shattering, and may be reported as "dust index" to the nearest whole per cent to indicate the relative dust-producing properties of coals when subjected to severe handling. Hence both the friability in per cent and the "dust index" may be reported as follows: Friability, per cent = 31.5; with dust index of 15.

is recommended that two or more four-jar tests be made. When only four single-jar tests are made, sieve the contents of each jar separately in order to be sure that there is satisfactory agreement between the results obtained. When two or more four-jar tests are made, the contents of the four jars from each set may be mixed and sieved together. Make the weighings to the nearest 1 g.

Report.—The results should be reported to the nearest 0.5% as friability, per

cent, which is the percentage reduction in average size of the coal during the tumbler test.

NOTE.—A numerical example of the method of calculating friability is given in Table 31-7, where the average of the openings of the retaining and passing sieves is expressed in inches to the nearest 0.001 in. The data shown are for a typical coal of medium friability. It is from the average of the sieve openings that the approximate relative size factors, shown as column (3) are derived. In the column to the extreme right,  $S$  represents the average size of the coal pieces before tumbling, and  $s$  the average size of the tumbled coal, the value for  $S$  being arbitrarily chosen as 100 times its corresponding size factor.

### SCREEN ANALYSIS OF COAL <sup>77</sup>

This method of test for screen analysis is applicable to all coal except anthracite, powdered coal as used in boiler plants, and crushed coal as charged into coke ovens.

*Apparatus.*—Screens of the following series should be used conforming to the Specifications for Sieves for Testing Purposes (ASTM Designation: E11, p. 1277).

#### *Round-Hole Screens:*

8-in.	3-in.	1½-in.	¾-in.
6-in.	2¼-in.	1¼-in.	½-in.
5-in.	2-in.	1-in.	⅜-in.
4-in.			

#### *Wire-Cloth Sieves with Square Openings:*

4760-micron (No. 4)	297-micron (No. 50)
2380-micron (No. 8)	149-micron (No. 100)
1190-micron (No. 16)	74-micron (No. 200)
590-micron (No. 30)	

*Time of Sampling.*—The coal should be sampled when it is being loaded into or unloaded from railroad cars, ships, barges, or wagons, or when discharged from supply bins, or from industrial railway cars, or grab buckets, or from any coal-conveying equipment, as the case may be. It is not feasible to collect representative samples for screen analysis from the surface of coal in piles or from loaded cars or bins.

*Collection of Gross Sample.*—Increments should be regularly and systematically collected, so that the entire quantity of coal sampled will be represented proportionately in the gross sample, and with such frequency that a gross sample of the required amount should be collected. The number of increments collected should be not less than 20. When the coal is passing over a conveyor or down a chute, increments the full width and thickness of the stream of coal should be taken either by stopping the conveyor and removing all coal from a transverse section of it, or by momentarily inserting a suitable container into the stream. If it is impracticable to collect increments the full width and thickness of the coal stream, increments should be systematically collected from all portions of the stream.

*Weight of Gross Sample.*—The weight of the gross sample collected should conform to the following:

<sup>77</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D410-38.

Run-of-mine coal. ....	not less than 4000 lb.
Screened coal with upper limit larger than 4-in. round .....	not less than 4000 lb.
Coal smaller than 4-in. round.....	not less than 2000 lb.
Coal smaller than 2-in. round.....	not less than 1000 lb.
Coal smaller than 1-in. round.....	not less than 500 lb.
Coal smaller than $\frac{1}{2}$ -in. round.....	not less than 100 lb.

**Reduction of Gross Sample.**—Reduction of the quantity of the gross sample should conform to the following:

(a) *Coal Larger than 1-in. Round.*—Coal larger than 1-in. round should be screened without mixing or reducing.

(b) *Coal Smaller than 1-in. Round.*—Coal smaller than 1-in. round may be reduced in amount to not less than 125 lb. by riffing or by arranging it in a long, flat pile and successively halving it or quartering it by the alternate-shovel method as follows: Take successive shovelfuls in passing around the pile (advancing a distance equal to the width of the shovel for each shovelful), and retain alternate shovelfuls or every fourth shovelful for the sample.

(c) *Coal Smaller than  $\frac{1}{2}$ -in. Round.*—Coal smaller than  $\frac{1}{2}$ -in. round may be reduced to not less than 25 lb. by passing it through a riffle or equally accurate reducing device, or by hand-quartering as described in the Method of Sampling Coke for Analysis (ASTM Designation: D346, p. 1260).

(d) *Coal Smaller than No. 4 Sieve.*—Coal smaller than the No. 4 sieve may be reduced to not less than 2 lb. by riffing or hand-quartering.

(e) *Coal Smaller than No. 8 Sieve.*—Coal smaller than the No. 8 sieve may be reduced to not less than 1 lb. by riffing or hand-quartering.

**Drying Sample.**—In case the coal is wet, the sample may be tested on screens 1-in. round and larger without drying, but the sample of coal smaller than 1-in. round (reduced in amount to 125 lb., as described in the preceding section, should be dried sufficiently to remove surface moisture which causes small particles to cling to the larger pieces. In cases of lignite, subbituminous, and high volatile C bituminous coals, care should be observed not to over-dry and cause weathering of the coal.

**Screen Analysis.**—The sample should be accurately weighed before screening. Starting with the largest screen, the sample should be screened in such increments as will allow the pieces to be in direct contact with the openings at the completion of the screening of each increment. The smallest screen through which all of the sample passes should be determined by actual test, in accordance with the following paragraphs:

*Coal Larger than  $2\frac{1}{2}$ -in. Round.*—Pieces of coal not passing readily through screens  $2\frac{1}{2}$ -in. round and larger should be tried by hand to see if they will pass through the openings in any position. Screens  $2\frac{1}{2}$ -in. round and larger should not be shaken except for whatever jiggling may be necessary to clear the screens of fine coal.

*Coal Smaller than  $2\frac{1}{2}$ -in. Round.*—Coal passing the  $2\frac{1}{2}$ -in. round screen should be tested with screens down to and including 1-in. round as follows: Move the screen horizontally a distance of about 8 in. at just sufficient rate to cause the pieces of coal to tumble or roll on the screen. Stop the motion of the screen without impact. After ten such shakes (five in each direction), screening of the increment should be considered complete.



*Coal Smaller than 1-in. Round.*—Coal passing the 1-in. round and smaller screens may be weighed and then reduced in amount as provided in the section on Reduction of Gross Sample, and then shall be dried as provided in the section on Drying. Screens smaller than 1-in. round should be shaken gently with a reciprocating horizontal motion until practically no more coal will pass through the openings. When both No. 100 and No. 200 sieves are used, the latter should be used first in order to facilitate screening.

*Report.*—The screen analysis results should be reported to the nearest 0.1% as follows:

	<i>Per Cent</i>
Retained on.....in. round.....	0
Retained on.....in. round, passing	
.....in. round.....	
.....	
.....	
.....	
Retained on No....., passing.....in.	
round.....	
Retained on No....., passing No.....	
Passing No.....	
Total.....	

If the sum of the weights shows a loss of over 2%, the analysis should be rejected and another test made.

## DESIGNATING THE SIZE OF COAL FROM ITS SCREEN ANALYSIS <sup>78</sup>

This method covers the designation of coal sizes from the results of screen analysis tests of samples taken to represent the condition of the coal as sold. The method applies only to natural continuous ranges of sizes as produced by mining, handling, crushing, screening, etc. In the case of special mixtures, or where the screen analysis indicates a substantial deviation from a normal gradation of sizes, a sufficiently complete screen analysis to properly describe the size composition should be made and reported in accordance with the Method of Test for Screen Analysis of Coal (ASTM Designation: D410, p. 1231).

This method does not cover the standardization of screens used in the commercial preparation of coal.

*Sampling and Screen Analysis.*—The sampling and screen analysis should be performed in accordance with the Method of Test for Screen Analysis of Coal (ASTM Designation: D410; see preceding section).

*Screens.*—Size designations should be in terms of screens of the following series, which screens should conform to the Specifications for Sieves for Testing Purposes (ASTM Designation: E11, p. 1277).

<sup>78</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as D431-44.

*Round-Hole Screens:*

8-in.	3-in.	1½-in.	¾-in.
6-in.	2½-in.	1¼-in.	½-in.
5-in.	2-in.	1-in.	⅜-in.
4-in.			

*Wire-Cloth Sieves with Square Openings:*

No. 4 (4760-micron)	No. 50 (297-micron)
No. 8 (2380-micron)	No. 100 (149-micron)
No. 16 (1190-micron)	No. 200 (74-micron)
No. 30 (590-micron)	

**Size Designation.**—The designation should indicate the range of the size by giving the upper and lower limiting screens between which more than 80 per cent of the sample is retained by actual test, the limiting screens being selected as follows:

(a) The screen defining the upper limit should be the smallest screen of the series given in the preceding section upon which is retained a total of less than 5% of the sample. The screen defining the lower limit shall be the largest screen of the series given in the preceding section through which passes a total of less than 15% of the sample.

(b) The terms for defining sizes should be written with the upper limiting screen first, followed by an "x" and that followed by the lower limiting screen. The abbreviation "in." should follow the lower limiting screen but may be omitted after the upper limiting screen. For screens of the U. S. standard sieve series (No. 4 and smaller), the abbreviation "No." should be used each time a screen is indicated. If the total retained on the 8-in. screen is 5% or greater, the size should be designated by the lower limiting screen preceded by the word "plus" and followed by an expression in parentheses giving the percentage over 8 in. to the nearest 1%.

(c) The following examples illustrate the system of size designation:

*Examples:*

plus ½ in. (10 per cent over 8 in.)  
 plus 4 in. (24 per cent over 8 in.)  
 plus No. 16 (6 per cent over 8 in.)  
 4 x 2 in.  
 3 x ½ in.  
 2 in. x No. 4  
 No. 4 x No. 30  
 1 in. x No. 50

**NOTES.**—On the basis of the relationship between square-mesh sieves and round-hole screens as determined by tests on coal, No. 4 sieve is roughly equivalent to ¼-in. round screen, No. 8 to ⅜-in. round, No. 16 to ½-in. round, and No. 30 to ⅝-in. round.

Anthracite is commonly tested at the point of preparation or preparation to determine whether the sizing conforms to the specifications of the Anthracite Committee of the Production Control Plan for the Anthracite Industry by means of a series of special round-hole screens adopted by the Anthracite Committee, none of which screens have the same size openings as the screens specified in the preceding section above. The methods of sampling and testing are given in the Method of Test for Size of Anthracite (ASTM Designation: D310; see following method).

SIZE OF ANTHRACITE <sup>79</sup>

This method of screen test for anthracite is intended for determining the percentage of undersize or oversize in any given commercial size.

**Screens.**—The screens for testing the various sizes of anthracite should consist of No. 16 U. S. gauge metal plates with staggered round openings. The screens should conform to the requirements for round-hole perforated plate screens prescribed in the Specifications for Sieves for Testing Purposes (ASTM Designation: E11, page 1277). Screens mounted in hardwood box frames 16 to 20 in. square are satisfactory for testing nut, pea, buckwheat, and rice sizes of anthracite. For broken, egg, and stove sizes, it is more convenient to use screens square or rectangular in shape having an area of 4 to 6 sq. ft. The screens may conveniently be mounted in a rack, so as to slide like drawers, with a pan underneath to catch the undersize.

**Screen Openings.**—The screen openings specified in the Anthracite Standards Law of the Commonwealth of Pennsylvania, effective September 1, 1949, as standard anthracite sizing specifications, are as follows:

Size	Size of Round-Hole Openings in Testing Screens, in.	
	Passing	Retained on
Broken.....	$4\frac{3}{8}$	$3\frac{1}{4}$ to 3
Egg.....	$3\frac{1}{4}$ to 3	$2\frac{7}{16}$
Stove.....	$2\frac{7}{16}$	$1\frac{5}{8}$
Nut.....	$1\frac{5}{8}$	$\frac{13}{16}$
Pea.....	$\frac{13}{16}$	$\frac{9}{16}$
Buckwheat.....	$\frac{9}{16}$	$\frac{5}{16}$
Rice.....	$\frac{5}{16}$	$\frac{3}{16}$

When testing coal to determine conformity with these specifications, these sizes of screen openings shall be used in the test.

**Unit for Sampling.**—Each carload or its equivalent shall be considered as a unit for sampling.

**Collection of Gross Sample.**—The gross sample should be not less than 200 lb. for broken and egg sizes, and not less than 100 lb. for stove, nut, pea, buckwheat, and rice sizes.

The gross sample should preferably be collected when the coal is being loaded or unloaded in accordance with the procedure described in the sections of the Methods of Sampling Coals Classed According to Ash Content (ASTM Designation: D492, p. 1137). The increments should be regularly and systematically collected, so that the entire quantity of coal sampled will be represented proportionately in the gross sample, and with such frequency that a gross sample of the required amount is collected. In case it is necessary to collect the sample from the exposed surface of the car, nine equal increments should be taken about one foot below the surface. The nine sampling points should be located as shown in Fig. 31-21.

<sup>79</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as D310-34.

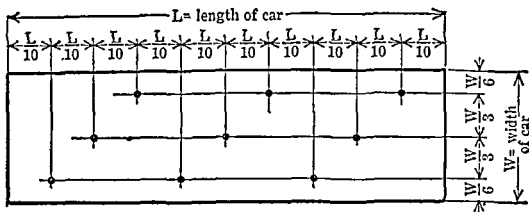


FIG. 31-21. Location of Sampling Points from Exposed Surface of Car.

**Preparation of Laboratory Sample.**—For broken, egg, stove, and nut sizes the gross sample should be screened without being mixed or reduced. For the pea size, the gross sample should be thoroughly mixed and reduced by quartering, without crushing, in accordance with the section on mixing and reduction of the Method of Sampling Coke for Analysis (ASTM Designation: D346, p. 1260). For the buckwheat and rice sizes, the gross sample should be thoroughly mixed and reduced by quartering, without crushing, in accordance with the same section of Method D346, or by passing through a riffle sampler in accordance with the relevant section of the Methods of Sampling Coals Classed According to Ash Content (ASTM Designation: D492, p. 1137). The laboratory samples should consist of the following approximate minimum amounts:

Size	Laboratory Sample, Approximate Minimum Weight, lb.
Pea . . . . .	50
Buckwheat . . . . .	25
Rice . . . . .	10

**Procedure.**—In case the coal is wet, air-dry it before screening. Determine the undersize first. For broken, egg, and stove sizes, upend each piece by hand on the screen, to determine whether in any position it passes through the screen. For nut, pea, buckwheat, and rice sizes, shake the screens gently with a reciprocating horizontal motion, so as to avoid breakage of the coal, until practically no more coal will pass through the openings. Screen the coal in such increments as will allow the pieces to be in direct contact with the screen openings after the completion of the shaking of each increment.

**Report.**—The undersize and oversize should be reported to the nearest 1%.

## SIEVE ANALYSIS OF CRUSHED BITUMINOUS COAL <sup>80</sup>

This method of test covers a procedure for the sieve analysis of rather coarsely crushed bituminous coal, less than 1.5 in. in size, such as is charged into coke ovens. It is not applicable to the testing of powdered coal as used in boiler plants.

<sup>80</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as D311-30.

100.0. However, if the sum of the weights retained on each sieve and that which passes the smallest sieve shows a loss of over 0.5%, the analysis should be rejected and another test made.

### CUBIC FOOT WEIGHT OF CRUSHED BITUMINOUS COAL<sup>81</sup>

This method of test covers two procedures for determining the cubic foot weight of crushed coal less than 1½ in. in size, such as is charged into coke ovens, as follows:

**Procedure A.**—The cone procedure for determining an uncompacted weight per cubic foot.

**Procedure B.**—The dropped-coal procedure for determining a compacted weight per cubic foot, comparable to actual bulk densities attained in coke ovens.

This method is not applicable to the testing of powdered coal as used in boiler plants, nor to the determination of weights per cubic foot of coal in storage piles.

#### PROCEDURE A.—CONE PROCEDURE FOR UNCOMPACTED CUBIC FOOT WEIGHT

**Apparatus. Measuring Box.**—A box of rigid construction should be provided, having inside dimensions of 12.0 by 12.0 by 12.0 in., and a volume of  $1728 \pm 5$  cu. in. The exact volume of the box should be determined by water calibrations.

**Cone.**—A cone, conforming to Fig. 31-22, should be provided for filling the box. This cone should be 2 ft. 0 in. high and 1 ft. 8 in. in inside diameter at the top, with a circular opening 4½ in. in diameter at the bottom. A slide valve consisting of a sliding-plate shutter and its supports should be welded to the bottom of the cone in such a manner that the valve may be opened and closed with ease by removing or inserting the shutter in its supporting slides. The cone should be supported in a tripod frame having a circular opening at the top of about 1 ft. 6 in. in diameter. This frame should support the cone so that the top-side of the shutter should be 1 ft. 10 in. from the inside bottom surface of the box.

**Leveling Bar.**—A leveling bar of steel strip 2 ft. 6 in. long by 1.5 in. wide and approximately ¾ in. thick should be provided.

**Scales.**—A platform scale, capable of weighing up to 200 lb. and sensitive to 0.1 lb., should be provided.

**Sampling. Gross Sample.**—For collecting gross samples of crushed bituminous coal, the procedure described in the relevant sections of the Methods of Sampling Coals Classed According to Ash Content (ASTM Designation: D492, p. 1137) should apply. During the period of collecting the gross sample, the increments of the sample should be stored in a waterproof container with a tightly fitting cover in order to prevent the loss of moisture. The minimum number and weights of increments collected shall be in accordance with Table 31-2 of Method D492, page 1139. The minimum gross weight of the sample should be 300 lb.

**Laboratory Sample.**—The gross sample of coal should be thoroughly mixed and subdivided, without crushing, into four 75-lb. portions. This operation should be done as quickly as possible to avoid loss of moisture, and the cubic foot weight should be determined immediately. If this determination cannot be made immediately, the samples should be kept in waterproof containers with tightly fitting covers until the time for making the determination.

<sup>81</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D291-60.

**Procedure.**—Before filling the cone hopper, level it in its tripod on a solid floor. Pour the prepared sample into a pile on the floor and carefully flatten it to about 4 in. in thickness. Avoid pounding of the pile with the back of the shovel. Take successive shovelfuls from uniformly distributed points in the pile, and allow them to slide gently from the shovel into the hopper at different peripheral points. This will prevent segregation and packing while the hopper is being filled. Place about 75 lb. of coal in the hopper.

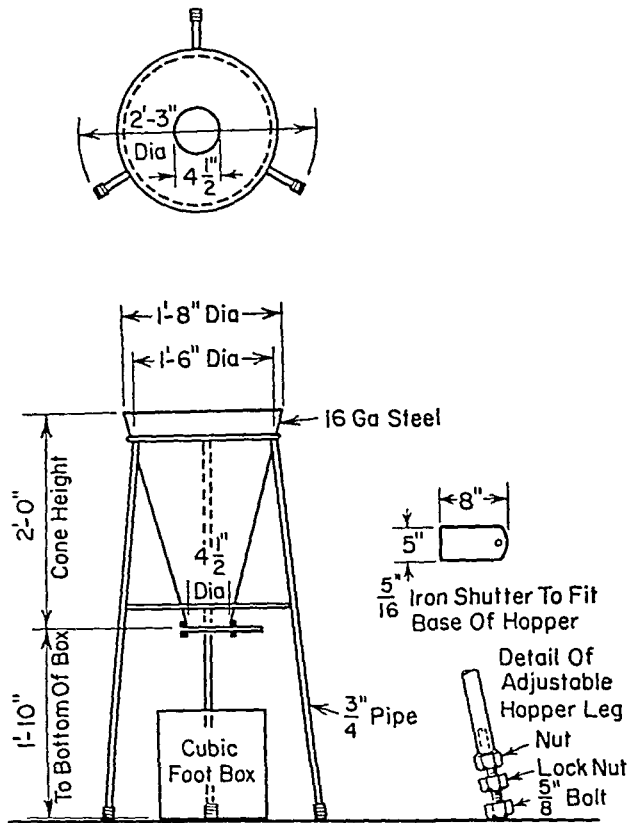


FIG. 31-22. Apparatus for Cone Procedure.

Center the previously weighed cubic foot box under the valve of the cone. Then remove the valve shutter completely, allowing all of the coal to flow into the box and overflow the edges. Loosen wet coal, not flowing freely from the hopper, by gently thrusting downward through the coal to the valve with the leveling bar.

After filling the box, carefully level off the excess coal above the box edge by means of the leveling bar, and place the box on the platform scale and weigh it to the nearest 0.1 lb. Avoid jarring or shifting of the filled box until all excess coal is leveled off. Record the difference in weight between the filled and empty box to the nearest 0.1 lb. as the uncompacted cubic foot weight.

**NOTE.**—Aside from the character of the coal itself, moisture content and size distribution of the coal are the two main factors which affect the cubic foot weight. A moisture determination and sieve analysis of the coal should be reported along with the cubic foot weight for proper interpretation of the cubic foot weight. For directions for making these determinations, see the following methods of the American Society for Testing and Materials:

**Moisture.**—Methods of Laboratory Sampling and Analysis of Coal and Coke (ASTM Designation: D271, p. 1150).

*Sieve Analysis.*—Method of Test for Sieve Analysis of Crushed Bituminous Coal (ASTM Designation: D311, p. 1236).

**Precision. Repeatability.**—Duplicate results by the same operator in a given laboratory on consecutive tests determined within a minimum interval of time shall be considered suspect if they differ by more than 0.6 lb. per cu. ft.

When two results are obtained that differ by more than this value, two additional tests shall be made. If the second pair of results differs by less than the repeatability, the first pair shall be discarded and the mean of the second pair shall be reported as the result of the test.

When both pairs of results exceed the repeatability, the mean of the four results shall be reported, provided that the two most divergent results differ by less than 1.32 times the repeatability of the procedure. Otherwise, all results shall be discarded and the apparatus, procedure, and sample shall be examined for non-compliance causes, which should be corrected before redetermining new pairs of values.

## PROCEDURE B.—DROPPED-COAL PROCEDURE FOR COMPACTED CUBIC FOOT WEIGHT <sup>82</sup>

**Apparatus. Measuring Box.**—A specially-constructed box, externally braced to ensure rigidity, should be provided, having inside dimensions of 18.0 by 24.0 by 8.0 in. high, and a volume of  $3456 \pm 10$  cu. in. The exact volume of the box should be determined by water calibration.

**Dropping Apparatus.**—A dropping apparatus, consisting of the shatter test machine described and illustrated in the Method of Drop Shatter Test for Coke (ASTM Designation: D141, p. 1268), should be provided. It should consist of a box 18 in. in width, 28 in. in length, and approximately 15 in. in depth, supported above a rigidly mounted cast-iron or steel plate, not less than 0.5 in. in thickness, 38 in. in width, and 48 in. in length. The inside of the bottom of the box should be 6 ft. above the plate. The bottom of the box should consist of two doors hinged lengthwise and latched so that they will swing open freely and not impede the fall of the coal. In order to facilitate filling the box with coal, the box should be constructed so that it can be lowered to a convenient level. This is best done by means of the arrangement shown in Fig. 31-23.

**Leveling Bar.**—A leveling bar of steel strip 2 ft. 6 in. long by 1.5 in. wide and approximately  $\frac{3}{16}$  in. thick should be provided.

**Scales.**—A platform scale capable of weighing up to 200 lb. and sensitive to 0.1 lb. should be provided.

**Sampling. Gross Sample.**—For collecting gross samples of crushed bituminous coal, the procedure described in the relevant sections of the Methods of Sampling Coals Classified According to Ash Content (ASTM Designation: D492, p. 1137), should apply. During the period of collecting the gross sample, the increments of the sample should be stored in a waterproof container with a tightly fitting cover in order to prevent the loss of moisture. The minimum number and weights of increments collected shall be in accordance with Table 31-2 of Method D492, p. 1139. The minimum gross weight of sample should be 800 lb.

**Laboratory Sample.**—The gross sample of coal should be thoroughly mixed and

<sup>82</sup> H. S. Auvil, L. S. Schmidt, and H. G. Graham, Control of Bulk Densities in Coke Ovens: Studies on Precision and Application of Various Testing Methods, U. S. Bureau of Mines R. I. 3935, 1946.





subdivided, without crushing, into four 200-lb. portions. This operation should be done as quickly as possible to avoid loss of moisture, and the cubic foot weight should be determined immediately. If this determination cannot be made immediately, the samples should be kept in waterproof containers with tightly fitting covers until the time for making the determination.

**Procedure.**—Place the previously-weighed measuring box on the floor of the dropping apparatus and center it directly under the hopper with the long axis of the box parallel to the long axis of the hopper. Mark the floor of the dropping apparatus so that the measuring box will always be positioned exactly the same each time.

Pour the prepared coal sample into a pile on the floor and carefully flatten it to about 4 in. in thickness. Avoid pounding of the pile with the back of the shovel. Take successive shovelfuls from uniformly distributed points in the pile, and carefully place them in the hopper to avoid segregation. Place each shovelful to one side of the preceding one until 180 to 200 lb. are contained in the hopper, avoiding any heaping up of the coal at any one point as well as any compacting of the coal with the shovel.

Raise the hopper containing the coal and allow the coal to drop into the measuring box from the 6-ft. height. Carefully level the excess coal even with the top edge of the box by means of the leveling bar. Avoid jarring or shifting of the filled box until all excess coal is leveled. Fill any voids left in the corners of the box below the top edge by gently raking the excess coal across the corner. Place the box, or its contents, on the platform scale and weigh it to the nearest 0.1 lb. Record the difference in weight between the filled and empty box to the nearest 0.1 lb. as the compacted cubic foot weight (see NOTE, p. 1239).

**Precision. Repeatability.**—Duplicate results by the same operator in a given laboratory on consecutive tests determined within a minimum interval of time shall be considered suspect if they differ by more than 1.0 lb. per cu. ft.

When two results are obtained that differ by more than this value, two additional tests shall be made. If the second pair of results differs by less than the repeatability, the first pair shall be discarded and the mean of the second pair shall be reported as the result of the test.

When both pairs of results exceed the repeatability, the mean of the four results shall be reported, provided that the two most divergent results differ by less than 1.32 times the repeatability of the procedure. Otherwise, all results shall be discarded and the apparatus, procedure, and sample shall be examined for non-compliance causes, which should be corrected before redetermining new pairs of values.

## INDEX OF DUSTINESS OF COAL AND COKE<sup>83</sup>

This method of test is intended for the determination of a relative index of the dust produced when handling coal or coke.<sup>84</sup>

<sup>83</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as D547-41.

<sup>84</sup> For information concerning the development of this method of test for index of dustiness of coal and coke, the following references may be consulted:

A. R. Powell and C. C. Russell, Method for Determining the Dustiness of Coal and Coke, Industrial and Engineering Chemistry, Analytical Edition, 5, September 15, p. 340, 1933; J. M. Pilcher and R. A. Sherman, The Treatment of Coal with Oil and Other

**Apparatus. Dust Cabinet.**—The apparatus consists of a metal cabinet 5 ft. in height and 18 in. square, inside dimensions, arranged with a cover and three slides, and a drawer at the bottom, as shown in Fig. 31-24. One slide should be inserted 12 in. below the top and forms the compartment into which the sample to be tested is placed. The other two slides should be inserted together 24 in. above the bottom and should serve to collect the settled dust after 2- and 10-min.

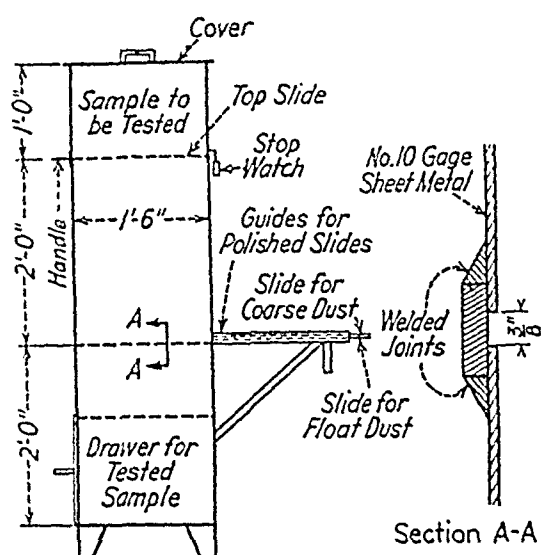


FIG. 31-24. Dustiness Test Cabinet.

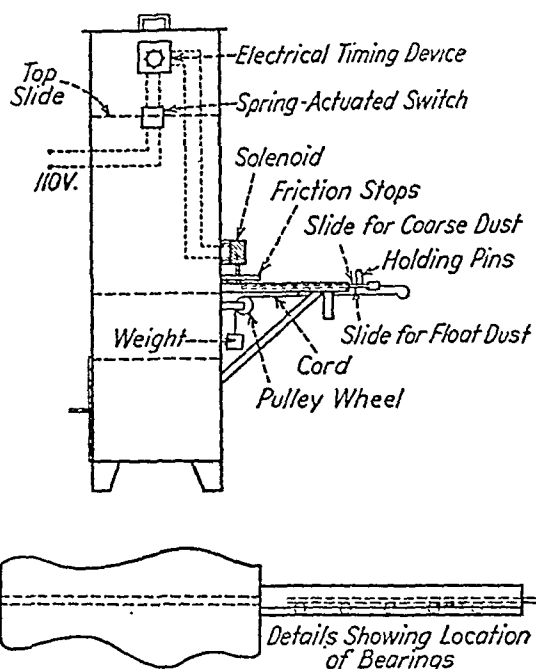


FIG. 31-25. Diagram of Equipment for Automatic Insertion of Slides.

intervals. Guides should be so constructed that the slides move easily, and the guides for the lower slides should extend 18 in. beyond one side of the cabinet. The lower slides should be inserted into the side opposite the side into which the top slide is inserted. A drawer 14 in. in depth should be located at the bottom for the removal of the sample. The entire apparatus should be dust-tight and constructed of nonrusting sheet metal such as galvanized iron. The cabinet may be made of No. 10 gauge sheet metal with edges bent over and welded. However, the bottom drawer may be made of No. 14 gauge metal to decrease the weight. All slides may be made of No. 8 gauge sheet metal. Each of the two lower slides should have a polished upper surface (for example, stainless steel, chromium plated brass, or plain polished steel). All slides should preferably be of the thickness specified but should be not less than No. 10 gauge to prevent bending and later binding in the guides. The inside surface of the cabinet should be smooth from the top to the lower slides.

**Optional Automatic Attachments.**—In order to increase the accuracy in timing of the insertion of the two lower slides, and to obviate the necessity for two persons being present at each test, an automatic means for the insertion of the slides may be added.

Figure 31-25 shows schematically the operation of the timing equipment. The spring-actuated switch closes when the top slide is halfway out. This starts the electrical timing device which closes a circuit at the end of a definite time interval and energizes a solenoid. The solenoid releases a weight<sup>85</sup> attached to the slides by a cord running over a ball-bearing pulley, which pulls the slides into the cabinet. The timing device shall be set so that 5 seconds elapse between the time that the upper slide is halfway out and that when the dust slides are halfway in. The time consumed in closing shall not exceed 0.5 second.

The solenoid also releases a vertical cover held over the slot in the cabinet for the insertion of the slides; this cover is required to prevent the loss of dust from the opening when the coal is dropped.

The connection between the slides and the cord attached to the weight and the pins that hold the slides together are readily removable so that the upper and lower slides may be removed independently after 2- and 10-min. intervals.

To reduce the friction of the slides on the guides, five double-sealed ball bearings are mounted on each guide to support the slides. The slides move in freely at an accelerated rate. To avoid the jar and rebound that would result if the slides were stopped on the back of the cabinet, a braking force is applied just before the slides reach the limit of their travel. Either of two schemes may be used for retarding the slides. In one method the braking force is applied through two leather-faced steel bars which bear on the pins that hold the slides together (Fig. 31-25). The contact of the brakes on the pins is so adjusted as to stop the slides  $\frac{1}{4}$  in. short of full travel. The operator gently pushes the slides in the remainder of the distance. Another method consists of retarding the slides by pneumatic compression cylinders having two adjustable vents, one for the initial retardment and the other to control the speed at which the slides seat themselves against the box.

**Sampling.**—The gross sample for the dustiness test shall be not less than 110 lb. of coal or coke. This is sufficient for duplicate tests.

**Method of Sampling.**—The gross sample should be collected in accordance with the procedures described in the Methods of Sampling Coals Classed According to Ash Content (ASTM Designation: D492, p. 1137) or the Method of Sampling Coke for Analysis (ASTM Designation: D346, p. 1260). The gross sample should be carefully collected so as to be representative with regard to size distribution; also, handling during collection should be such as to minimize breakage of pieces. If an index of dustiness at time of sampling is desired, the sample should be accumulated in a waterproof container with a tight-fitting cover.

**Sample Preparation.**—As soon as possible after collection, the gross sample should be reduced to two samples of approximately  $50 \pm 2.5$  lb. each, by the alternate shovel procedure as described in the Method of Sampling Coke for Analysis (ASTM Designation: D346, p. 1260). By reducing the gross sample in this manner, *prior* to air-drying, the loss of float-dust is minimized, especially in cases where the samples may be damp. Segregation is also less when reducing a damp sample.

**Drying Procedure.**—If it is desired to determine the index of dustiness of the coal or coke at the time of sampling, no drying is required and the material, as sampled, is ready for test which should be made as soon as practicable after collection of the sample.

<sup>85</sup> The size of the weight is dependent upon weight of dust slides and amount of friction in pulling slides into cabinet.

If it is desired to determine the index of dustiness which may develop when the coal or coke is stored under dry conditions, such as in the basement of a purchaser, air-dry the sample so as to approximate the air conditions of the stored fuel. Either of the following two drying procedures may be used:

(1) Spread the 50-lb. samples out in flat-bottomed tared pans, weigh, and then allow to stand in a warm dry room whose atmosphere is free of entrained dust and where there are no appreciable air currents. Continue the drying until the rate of loss is less than 0.1% per hour.

(2) Place the samples in a large air-drying oven similar to that used for air-drying samples for chemical analysis.<sup>86</sup> Spread the 50-lb. samples out in a thin layer in flat-bottomed tared pans, weigh, and then dry in the air-drying oven at not more than 15°C. above room temperature. Stir and weigh the samples at intervals. Continue drying until the rate of loss is less than 0.1% per hour. One to three days will be required, depending upon the moisture content of the sample at the time that it is placed in the drier.

**Procedure.**—Before each test, brush the inside surfaces, all slides, bottom drawer, and top cover of the apparatus free of dust. Then insert the top slide to form the upper compartment. Place the 50-lb. sample, prepared in accordance with the two preceding sections, in the upper compartment, level off the top of the sample, and close the top cover tightly. In placing the sample in the top of the cabinet, care should be taken to avoid excessive segregation. Then place the two polished slides, which have been brushed free of dust, on the guide extension, ready for insertion. The bottom drawer should be tightly in place. When all is in readiness, withdraw the upper slide with a quick motion, thus allowing the sample to drop into the drawer. Exactly 5 seconds later, as indicated by a stop watch, quickly insert both lower slides. It is of particular importance that the slides be pushed in at exactly 5 seconds after the sample is dropped, because the larger pieces of dust are dropping rapidly at the time, and a slight difference in the time of insertion of the slides will make a considerable difference in the amount of dust collected. After the slides have stood undisturbed for 2 min. from the time of insertion, withdraw the top of the two lower slides, and then, after the other slide has stood undisturbed for an additional 8 min. withdraw it. Keep the dust on each slide separate and, in order to remove the dust, place each slide on a stand so that one side extends over a glass funnel about 5 in. in diameter, supported in a ring stand with a weighing bottle below the funnel outlet. Carefully brush the dust into the funnel so that it falls directly into the weighing bottle. Then determine the weight to the nearest 0.001 g. The dust for the first period is designated “coarse dust,” and that for the second period is called “float dust.”

**Number of Tests.**—All tests shall be made in duplicate and the average value reported as the dustiness index.

**Calculation.**—The index of dustiness shall be calculated as follows:

Dustiness index, coarse dust =  $40 \times$  weight of dust in grams settled after 2 min.

Dustiness index, float dust =  $40 \times$  weight of dust in grams settled next 8 min.

**NOTE.**—The dust from the slides must not be assumed to be the total amount of dust in the sample. The method is entirely empirical but it gives a measure of the dust produced when handling coal or coke.

<sup>86</sup> See Fig. 31-3 of the Methods of Laboratory Sampling and Analysis of Coal and Coke (ASTM Designation: D271), see p. 1146.

**Expression of Index Values.**—The following general rules shall govern the use of significant figures in the expression of results:

(a) If the index values are less than 10, only one decimal place shall be recorded.

(b) If the index values are 10 or greater, only whole numbers shall be recorded.

**Reproducibility of Results.**—With proper care and strict attention to details, the difference between duplicate tests shall not exceed 20% of the average index value. If the difference is larger than 20%, additional samples shall be obtained and tested.

## PLASTIC PROPERTIES OF COAL BY THE GIESELER PLASTOMETER <sup>87</sup>

This method of test covers a *semi-quantitative* procedure for determining the *relative* plastic behavior of coal when heated under prescribed conditions in the absence of air.<sup>88</sup> The test may be used when studying coals and blends used in carbonization and in other situations where plastic properties are of practical importance.

**Apparatus.**—A convenient form of the Gieseler plastometer is shown schematically in Fig. 31-26. The apparatus consists of the following:

**Retort.**—A steel retort consisting of five parts as shown in Fig. 31-27 should be provided:

(1) *Retort Crucible*, cylindrical,  $0.844 \pm 0.003$  in. in inside diameter and 0.625 in. in depth, with exterior threads for joining the crucible to the barrel.

(2) *Barrel*, at least 6 in. long and having an inside diameter of  $0.375 \pm 0.003$  in. except at the crucible end where it should have an inside diameter of  $0.844 \pm 0.003$  in. to a height of 0.500 in. above the threads as shown. The total depth of retort chamber should be not greater than 1.25 in. The top end of the barrel should be 0.625 in. in inside diameter to a depth sufficient to allow clearance for the axle of the plastometer head when the apparatus is assembled. A hole, fitted with a tube, should be provided at a point at least two thirds the length of the barrel above the crucible so as to afford exit for the volatile products during a test.

(3) *Steel Washer*,  $0.0625 \pm 0.001$  in. in thickness and containing a central opening  $0.375 \pm 0.002$  in. in diameter as shown in Fig. 31-27.

(4) *Steel Stirrer*, as shown in Fig. 31-27, provided with a straight shaft of  $0.156 \pm 0.001$  in. in diameter and equipped with four rabble arms. The lower end of the stirrer should be tapered to a point having an included angle at least  $10^\circ$  greater than that of the notch in the bottom of the crucible. The rabble arms on the stirrer should be  $0.0625 \pm 0.001$  in. in diameter,  $0.250 \pm 0.002$  in. in length, and should be placed perpendicular to the shaft at  $90^\circ$  intervals around the shaft and  $0.125 \pm 0.001$  in. apart center to center along the shaft. The middle two rabble arms should be set at  $180^\circ$  to each other, and likewise the remaining two arms

<sup>87</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D1812-60T.

<sup>88</sup> For information concerning the experimental work on which this method is based, the following references may be consulted: R. E. Brewer and J. E. Triff, *Measurement of Plastic Properties of Bituminous Coals*, Industrial and Engineering Chemistry, Analytical Edition, 11, p. 242, 1939; G. C. Soth and C. C. Russell, *The Gieseler Method for Measurement of the Plastic Characteristics of Coal*, Proceedings, Am. Soc. Testing Mats., 43, p. 1176, 1943.

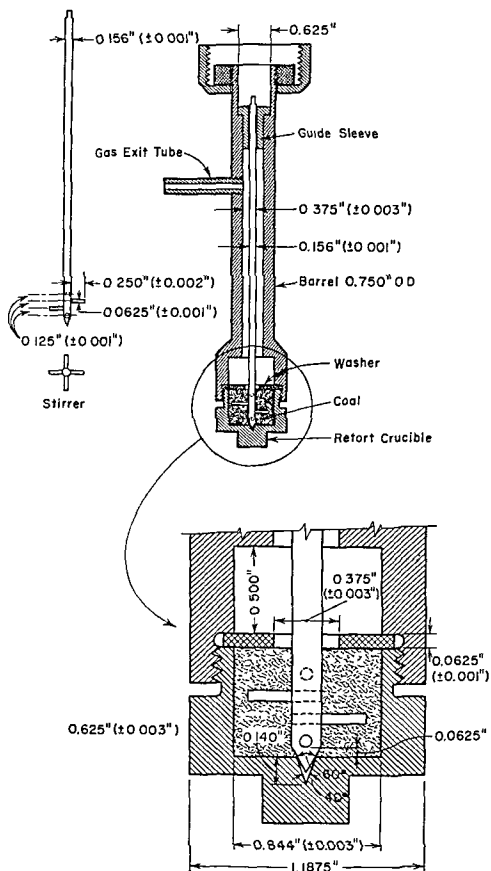


FIG. 31-27. Retort Assembly.

indicate movement on a concentrically mounted round dial divided into 100 divisions for the 360 degrees. The end of the cord should be loaded with a total weight of 40 g.

**Furnace.**—An electrically-heated furnace with suitable manual or automatic controls should be provided so that a heating rate of  $3.0^{\circ} \pm 0.1^{\circ}\text{C.}$  per minute on an overall basis with not more than  $3.0^{\circ} \pm 1.0^{\circ}\text{C.}$  per any 1 minute can be maintained over the range of  $300^{\circ}$  to  $550^{\circ}\text{C.}$  The furnace should contain a molten solder

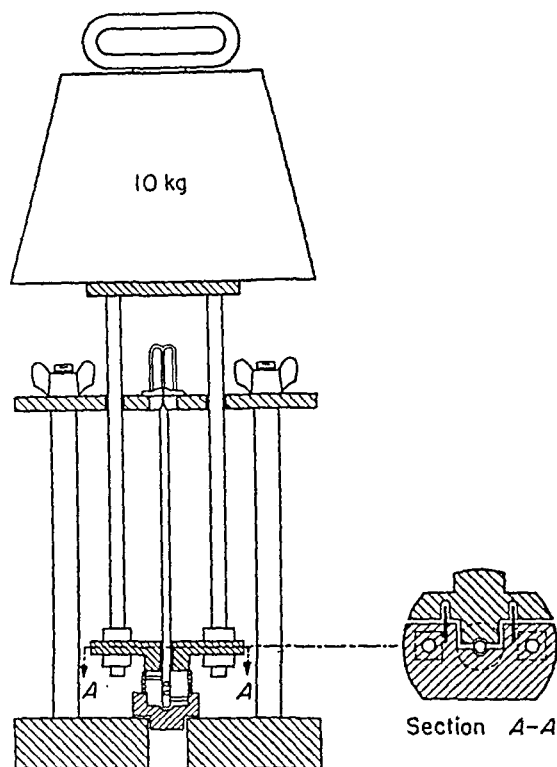


FIG. 31-28. Loading Device.

bath of approximately 50% lead and 50% tin composition or equivalent. Temperatures in the bath should be measured with a suitable thermocouple in a  $\frac{1}{4}$ -in. outside diameter protection tube immersed in the bath so that the tube touches the outside wall of the crucible and the hot junction of the couple is at the same height as the center of the coal charge. A stirrer may be used to agitate the solder. A suitable furnace is illustrated in Fig. 31-26.

**Loading Device.**—The loading device should be provided so that the coal may be packed uniformly in the crucible under a total packing load of 10 kg. and designed in such a manner that after compression the crucible and its contents can easily be removed from the device without disturbing the contents. A suitable device is shown in Fig. 31-28.

**Sample.**—A representative gross sample of coal should be collected and prepared in accordance with the Methods of Sampling Coals Classed According to Ash Content (ASTM Designation: D492, p. 1137). Approximately 15 lb. of coal crushed to pass a No. 4 ( $4760 \mu$ ) sieve should constitute the laboratory sample.

**Preparation of Sample.**—Air-dry the sample prior to preparation. Spread the sample on tared pans, weigh and air-dry it at room temperature or at slightly

Place the thermocouple in the bath as directed under *Furnace* (p. 1249), and cover the bath with a piece of transite. The heating control shall be such that the bath will reattain the initial temperature in  $10 \pm 2$  min. after immersion of the retort. Thereafter, heat the retort at a rate of  $3.0^\circ \pm 0.1^\circ\text{C.}$  per min. on the overall basis.

When the retort has attained the initial bath temperature, set the brake on the drum pulley in a released position and set the dial pointer at zero. At the first detectable continuous movement of the pointer as defined below under *Report*, record the corresponding temperature as the "initial softening temperature." Thereafter, take the reading of time, temperature, and pointer movement at 1-min. intervals. If the rate of turning of the pointer becomes such that the length of cord on the drum pulley will not permit completion of the determination, apply the brake and rewind the cord on the pulley. Periodically, at 1-min. intervals, release the brake and determine the rate of pointer movement by means of a stopwatch. Take care to allow the pointer to reach a uniform movement before timing and to obtain a time interval as long as is conveniently possible in order to increase the accuracy. Make these periodic readings until the pointer movement becomes such that after releasing the brake the length of cord remaining on the drum pulley will permit the completion of the determination. Continue readings until the pointer shows no further movement. When it is necessary during the test to rewind the cord on the drum pulley, take care not to disturb the stirrer in the coal sample.

**Number of Tests.**—All tests shall be made in duplicate and the average values reported.

**Care of Plastometer.**—It is most important that the dimensions of the rabble arms on the stirrer meet the specifications under *Steel Stirrer* (p. 1246), and Fig. 31-27. In addition to thorough cleaning of the stirrer and crucible between tests, it is important that the dimensions of the rabble arms be checked at frequent intervals. The total surface area of the four rabble arms, when new, should be approximately 0.21 sq. in. When, after use, it is found by accurate measurement that the area is 0.18 sq. in. or less, the rabble arms shall be replaced or the entire stirrer discarded.

The ball bearings shall be thoroughly cleaned in a light solvent at frequent intervals. Before reassembly they should be lubricated with a high-temperature, low-viscosity, silicone oil. Three drops of oil should be used per bearing and the oil distributed uniformly over the balls.

**Report.**—From the observed times and dial readings the corresponding movement of the pointer shall be calculated in dial divisions per minute. All values over 15,000 shall be reported as "greater than 15,000 divisions per minute." Bituminous coals show a wide range of fluidities. For this reason it is convenient to plot dial divisions per minute as ordinates on a logarithmic scale against temperatures as abscissas on an arithmetic scale.

The report shall also include the following:

(1) *Initial Softening Temperature.*—The temperature at which the dial pointer movement reaches 0.5 dial divisions per min. It is permissible to characterize this temperature by other dial divisions per minute, but in these cases it shall be reported as such.

(2) *Maximum Fluid Temperature.*—The temperature at which the dial pointer movement reaches the maximum rate.



(3) *Solidification Temperature*.—The temperature at which the dial pointer movement stops.

(4) *Maximum Fluidity*.—The maximum rate of dial pointer movement in dial divisions per minute.

Certain coals have the tendency to swell up into the barrel during the determination. Upon completion of the test and after cooling, the retort shall be carefully disassembled and the amount of material remaining in the crucible and attached to the rabble arms shall be recorded.

*Reproducibility*.—All characteristic temperature points for duplicate tests should agree within 5°C. Maximum rate of pointer movement should agree within 20%.

## FREE SWELLING INDEX OF COAL<sup>90</sup>

This method<sup>91</sup> is a small-scale laboratory test for obtaining information regarding the free-swelling properties of a coal; the results may be used as an indication of the coking characteristic of the coal when burned as a fuel. This test is not recommended as a method for the determination of expansion of coals in coke ovens.

*Apparatus. Burner Assembly*.—A gas burner with a large grid (external diameter  $1\frac{3}{16}$  in.), a draft shield, and a triangular crucible support as shown in Figs. 31-29 and 31-30. The draft shield, conforming to the dimensions shown in Fig. 31-29, should be made from asbestos cement pipe, and at the top it should have three slots, 1 in. in depth, in which the wires of the crucible support rest. The draft shield should be supported on a ring stand, so that the distance between the base of the crucible and the top of the burner grid may be adjusted by raising or lowering the draft shield. The triangular crucible support should be made of three pieces of translucent silica tubing each 63 to 64 mm. in length and 6 to 6.5 mm. in external diameter and mounted on chromium-nickel wire so that the diameter of the inscribed circle is approximately 32 mm. The twisted ends of the triangle may be joined together by a loop of wire in order to facilitate removal of the hot crucible.

*Crucibles*.—At least four translucent silica, low-form crucibles, with silica, ring-handle lids, conforming to the following requirements; also an extra pierced lid for determining the crucible temperature:

Weight, g . . . . .	11.0 to 12.75
External height, mm. . . . .	26 ± 0.5
External diameter at top, mm . . . . .	41 ± 0.75
Internal diameter at base, min., mm. . . . .	11
Capacity (approximate) cu. cm . . . . .	17

*Flow Meter*.—A capillary flow meter with water manometer placed in the gas line before the burner as a guide to the control of the rate of gas flow (Fig. 31-29).

<sup>90</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D720-57.

<sup>91</sup> This method is an adaptation of the Crucible Swelling Test for Coal, of the British Standards Institution. For information concerning the experimental work on which this adaptation is based, see paper by H. N. Ostborg, H. R. Limbacher, and Ralph A. Shermau, *An Experimental Investigation of the British Standard Method for the Crucible Swelling Test for Coal*, Proceedings, Am. Soc. Testing Mats., 42, p. 851, 1942. See also a paper by W. A. Selvig and W. H. Ode, *An Investigation of a Laboratory Test for Determination of the Free-Swelling Index of Coal*, Revision of R. I. 3989, U. S. Bureau of Mines Report of Investigation 4238, 1948.

**Sight Tube.**—A sight tube, as shown in Fig. 31-30, for viewing the coke buttons so that the effect of parallax will be eliminated. The tube should be made of either glass or metal tubing, and supported vertically on a ring stand.

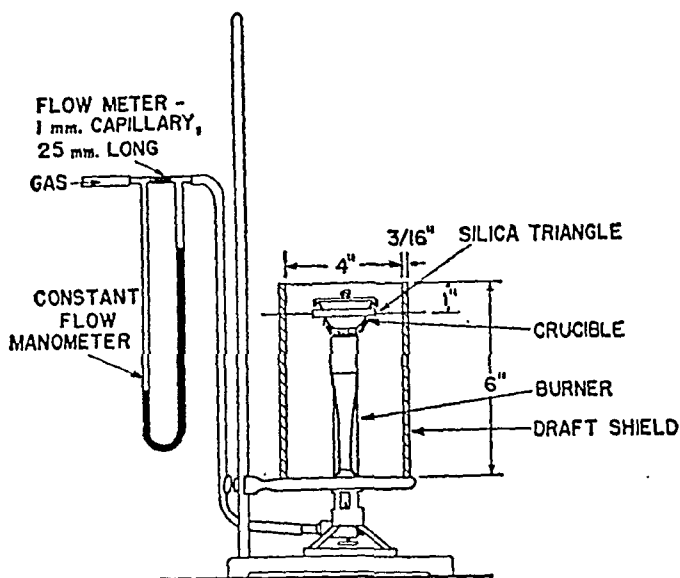


FIG. 31-29. Details of Burner Assembly.

**Preparation of Sample.**—The sample of coal should be freshly ground to pass a 250-micron (No. 60) sieve, and it should be prepared in accordance with the requirements of the Standard Methods of Laboratory Sampling and Analysis of Coal and Coke (ASTM Designation: D271, see p. 1145).

**Calibration of Burner.**—With the burner assembly arranged as shown in Fig. 31-29, and with a blank crucible in position, the burner should be lighted about 15 min. before making a determination to allow the draft shield to rise to an equilibrium temperature. The flow of gas and the relative positions of the burner and the draft shield should then be so adjusted that the temperature of the inner surface of the bottom of the crucible reaches  $800^{\circ} \pm 10^{\circ}\text{C.}$  in 1.5 min. and  $820^{\circ} \pm 5^{\circ}\text{C.}$  in 2.5 min., after placing a crucible in position. These desired temperatures may usually be obtained by setting the draft shield so that the bottom of the crucible is approximately  $\frac{3}{8}$  in. above the burner grid, and then adjusting the gas flame. The crucible temperature should be determined by means of a thermocouple of No. 28 gauge chromel-alumel wire and a potentiometer. The thermocouple should be inserted through the pierced crucible lid so that the unprotected junction of the thermocouple and a portion of each wire are in contact with the base of the crucible.

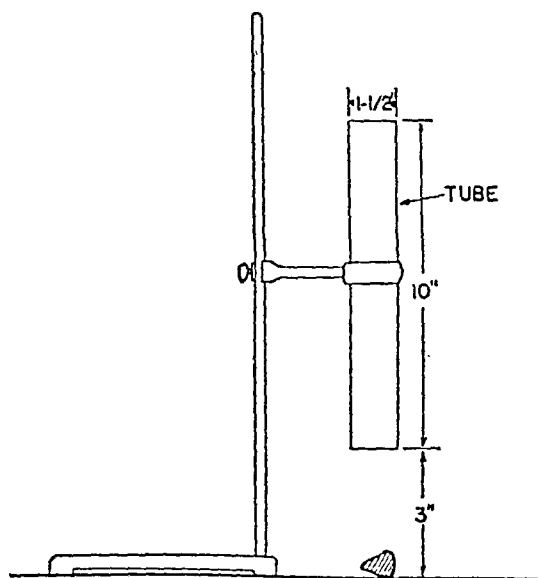


FIG. 31-30. Sight Tube.

**Procedure.**—One gram of the prepared sample should be weighed in a cold crucible, and the coal leveled by lightly tapping the crucible 12 times on a solid surface, rotating it between taps. The crucible should then be covered with a lid and placed upright in the silica triangle supported in the draft shield, directly over the gas flame. The covered crucible should be heated in the gas flame for the time required for the flame of the burning volatile matter to die out, but in any case for not less than 2.5 min. The coke button should then be carefully removed, and the carbon residue remaining in the crucible removed by ignition. Four buttons should be made in this manner for each sample of coal tested.

Each coke button should be viewed through the sight tube and compared with the series of standard profiles shown in Fig. 31-31. The standard profile with which a button is to be compared should be placed exactly in the center of the field of vision as viewed from the top of the tube. The button should then be placed on the profile and rotated on its axis until, as viewed with the eye placed immediately over the top of the tube, the maximum cross-sectional area is obtained. The number of the standard profile most nearly matched by the maximum cross-sectional area of the button should be recorded as the swelling index. If any button deviates by more than 1 unit from the other three buttons, a new determination should be made.

Some coals give buttons that do not conform in shape to the standard profiles. For such coals, the maximum cross-sectional areas of the buttons may be measured, and the index determined from the relationship of the areas of the standard profiles to swelling indexes as shown in Fig. 31-32.<sup>92</sup> For measuring the cross-sectional areas, the buttons may be mounted on graph paper ruled into square centimeters and square millimeters, and the outlines of the buttons traced on the paper while viewing through the sight tube shown in Fig. 31-30. The mounting of the buttons may be done conveniently by means of modeling clay. The squares inside the outline may be counted, and fractions of squares along the boundary line estimated.

**Report.**—Report the average swelling index of the series of four buttons, expressed to the nearest one-half unit.

If the residue is a powder or if the button is non-swollen (swelling index of 1) and pulverizes under a weight of 500 g. carefully lowered on it, designate the coal as "nonagglomerating."

### CLASSIFICATION OF COALS BY RANK <sup>93</sup>

These specifications cover the classification of coals by rank, that is, according to their degree of metamorphism, or progressive alteration, in the natural series from lignite to anthracite.

**Basis of Classification.**—The basic scheme of classification is according to fixed carbon and calorific value (expressed in Btu) calculated to the mineral-matter-free basis. The higher-rank coals are classified according to fixed carbon on the dry basis; and the lower-rank coals according to Btu on the moist basis. Agglomerating and slacking indices are used to differentiate between certain adjacent groups.

<sup>92</sup> To take care of buttons whose cross-sectional area is greater than that of standard profile 9, the curve shown in Fig. 31-32 has been extended to include about 700 sq. mm., which is the maximum cross-sectional area of the silica crucibles used in the test.

<sup>93</sup> Under the standardization procedure of the Society, these specifications are under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D388-38.

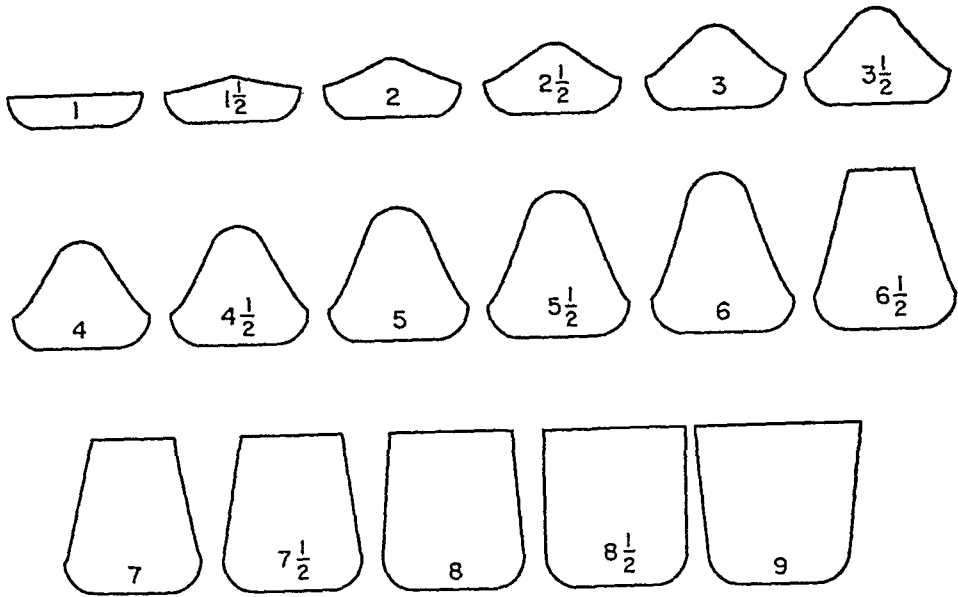


FIG. 31-31. Full-Scale Standard Profiles and Corresponding Swelling Index Numbers.  
(Courtesy of British Standards Institution.)

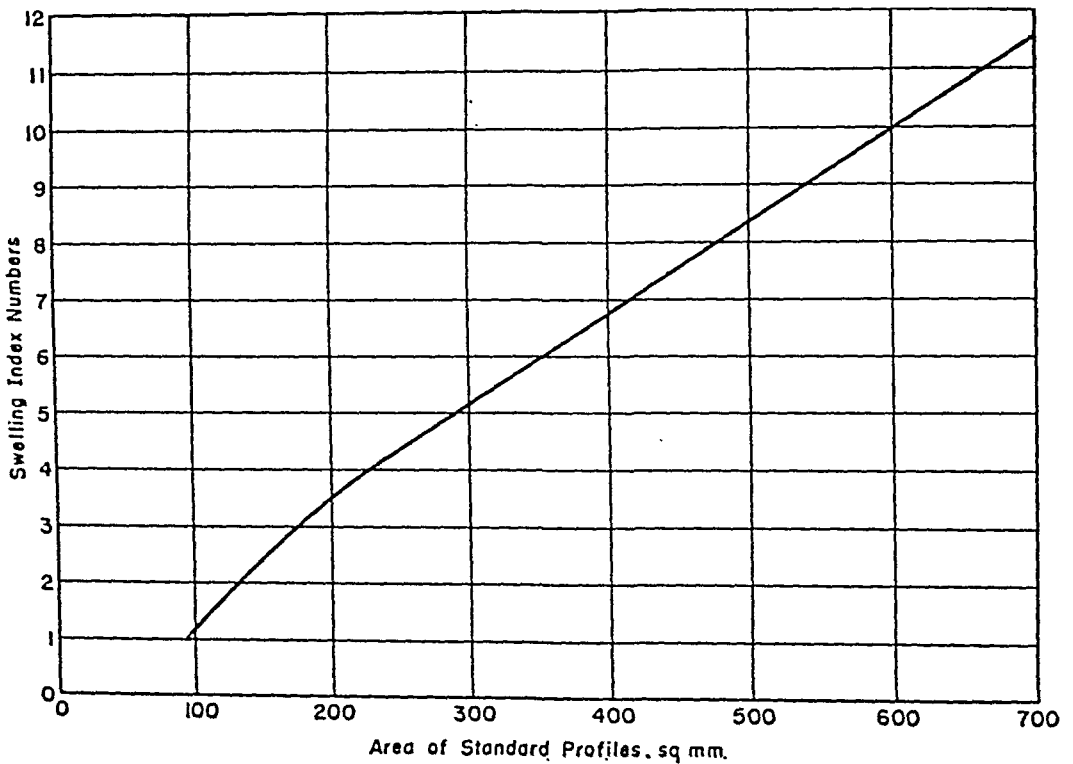


FIG. 31-32. Relationship of Areas of Standard Profiles to Swelling Indexes.

## CLASSIFICATION BY RANK

**Classification by Rank.** (a) *Fixed Carbon and Btu.*—Coals should be classified by rank in accordance with Table 31-8. Coals having calorific values of 14,000 Btu or more on the moist, mineral-matter-free basis, and coals having fixed carbon of 69% or more on the dry, mineral-matter-free basis, should be classified according to fixed carbon on the dry, mineral-matter-free basis; coals having calorific values less than 14,000 Btu on the moist, mineral-matter-free basis should be classified according to Btu on the moist, mineral-matter-free basis, provided the fixed carbon on the dry, mineral-matter-free basis is less than 69%.

(b) *Weathering Index.*—Coals showing average weathering indexes of less than 5% should be considered nonweathering; coals showing average weathering indexes of 5% or more should be considered weathering from the standpoint of classification.

(c) *Agglomerating Index.*—Coals which in the volatile matter determination produce either an agglomerate button that will support a 500-g. weight without pulverizing, or a button showing swelling or cell structure, should be considered agglomerating from the standpoint of classification.

**Symbols for Expressing Classification.**—(a) The position of a coal in the scale of rank may be expressed in condensed form as in the following example:

$$(62 - 146)$$

in which the parentheses signify that the contained numbers are on the mineral-matter-free basis. The first number represents fixed carbon on the dry basis, reported to the nearest whole per cent. The second number represents Btu on the moist basis, expressed as hundreds of Btu (to the nearest hundred); for example, 14,580 Btu would be represented as 146.

(b) When agglomerating or weathering properties enter into the classification of a coal, they should be expressed outside and immediately following the parenthesis by the following symbols:

ag = agglomerating  
na = nonagglomerating  
we = weathering  
nw = nonweathering

(c) *Classification by Grade and Rank.*—When the classification of a coal is reported according to both grade and rank, the grade designation should follow the rank designation as illustrated in the following example:

$$(62 - 146), 4 \times 2 \text{ in.}, 132 - A8 - F24 - S1.6$$

**NOTE.**—The numbers in parentheses show the position of a coal in the scale of rank and are on the mineral-matter-free basis, as expressed in the first paragraph of this section. The numbers and symbols following the parenthesis show the position of a coal according to classification by grade expressed in accordance with the relevant section of the Specifications for Classification of Coals by Grade (ASTM Designation: D389), and indicate a coal of 4 x 2-in. size designation, having a calorific value of approximately 13,200 Btu, an ash of 6.1 to 8.0%, inclusive, an ash-softening temperature of 2400 to 2590°F., inclusive, and a sulfur content of 1.4 to 1.6%, inclusive.

**Sampling. Bed Samples.**—The classification of a coal bed, or part of a coal bed, in any locality should be based on the average analysis and calorific value

TABLE 31-8. CLASSIFICATION OF COALS BY RANK <sup>a</sup>

Legend: FC = Fixed Carbon      VM = Volatile Matter      Btu = British thermal units

Class	Group	Limits of Fixed Carbon or Btu Mineral-Matter-Free Basis	Requisite Physical Properties
I. Anthracitic	1. Meta-anthracite	Dry FC, 98% or more (Dry VM, 2% or less)	Nonagglomerating <sup>b</sup>
	2. Anthracite.....	Dry FC, 92% or more and less than 98% (Dry VM, 8% or less and more than 2%)	
	3. Semianthracite	Dry FC, 86% or more and less than 92% (Dry VM, 14% or less and more than 8%)	
II. Bituminous <sup>d</sup>	1. Low volatile bituminous coal	Dry FC, 78% or more and less than 86% (Dry VM, 22% or less and more than 14%)	Either agglomerating or nonweathering <sup>f</sup>
	2. Medium volatile bituminous coal	Dry FC, 69% or more and less than 78% (Dry VM, 31% or less and more than 22%)	
	3. High volatile A bituminous coal	Dry FC, less than 69% (Dry VM, more than 31%); and moist <sup>e</sup> Btu, 14,000 <sup>e</sup> or more	
	4. High volatile B bituminous coal	Moist <sup>e</sup> Btu, 13,000 or more and less than 14,000 <sup>e</sup>	
	5. High volatile C bituminous coal	Moist Btu, 11,000 or more and less than 13,000 <sup>e</sup>	
III. Subbituminous	1. Subbituminous A coal	Moist Btu, 11,000 or more and less than 13,000 <sup>e</sup>	Both weathering and nonagglomerating
	2. Subbituminous B coal	Moist Btu, 9500 or more and less than 11,000 <sup>e</sup>	
	3. Subbituminous C coal	Moist Btu, 8300 or more and less than 9500 <sup>e</sup>	
IV. Lignitic	1. Lignite.....	Moist Btu, less than 8300	Consolidated Unconsolidated
	2. Brown coal....	Moist Btu, less than 8300	

<sup>a</sup> This classification does not include a few coals which have unusual physical and chemical properties and which come within the limits of fixed carbon or Btu of the high-volatile bituminous and subbituminous ranks. All of these coals either contain less than 48% dry, mineral-matter-free fixed carbon or have more than 15,500 moist, mineral-matter-free Btu.

<sup>b</sup> If agglomerating, classify in low-volatile group of the bituminous class.

<sup>c</sup> Moist Btu refers to coal containing its natural bed moisture but not including visible water on the surface of the coal.

<sup>d</sup> It is recognized that there may be noncoking varieties in each group of the bituminous class.

<sup>e</sup> Coals having 69% or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of Btu.

<sup>f</sup> There are three varieties of coal in the high-volatile C bituminous coal group, namely: Variety 1, agglomerating and nonweathering; Variety 2, agglomerating and weathering; Variety 3, nonagglomerating and nonweathering.

(and agglomerating and weathering index where required) of not less than three and preferably five or more face samples taken in different and uniformly distributed localities, either within the same mine or closely adjacent mines representing a continuous and compact area not greater than approximately four square miles in regions of geological uniformity. In regions where conditions indicate that the coal probably varies rapidly in short distances, the spacing of samples and grouping of analyses to provide average values should not be such that coals of obviously different rank will be used in calculating average values.

The samples should be taken in accordance with the U. S. Bureau of Mines method<sup>94</sup> or its equivalent, and shall be placed in moisture-tight containers in the mine.

Analyses of samples from outcrops or from weathered or oxidized coal should not be used for classification by rank.

In case the coal is likely to be classified on the "moist" basis, that is, containing the natural bed moisture, the samples should be taken at freshly exposed faces which are free from visible surface moisture if possible. Samples of low-rank coals which appear dry at the time of collection frequently give off moisture which condenses on the inner surface of the sample containers before they are opened for analysis. In the case of coals which were free from visible surface moisture when sampled, but which show moisture on the inner surface of the containers when opened, both the container and the coal should be weighed before and after air-drying, and the total loss in weight should be reported as air-drying loss.

If it is impossible to sample the coal without including visible surface moisture, and the coal is likely to be classified on the "moist" basis, the sampler should include the following statement in the description: "Sample contains surface moisture." Samples so marked should not be used for classification on a moist basis unless brought to a standard condition of moisture equilibrium at 30°C. in a vacuum desiccator containing a saturated solution of potassium sulfate (97% humidity) as suggested by Stansfield and Gilbert.<sup>95</sup> Analyses of such wet samples which have been treated in this manner shall be designated as "wet samples equilibrated at 30°C. and 97% humidity."

**Tipple or Shipment Samples.**—The classification of "run of mine" coal and prepared sizes of coal should be based on representative samples taken in accordance with the Methods of Sampling Coals Classified According to Ash Content (ASTM Designation: D492, p. 1137).

In case the coal is likely to be classified on the "moist" basis, the samples should be taken at the tipple or preparation plant and protected against loss of moisture as specified in the relevant section of Methods D492. Samples which appear dry at the time of collection shall be handled in accordance with the fourth paragraph of the section above on sampling to ensure correct determination of total air-drying loss. Samples which have visible surface moisture on the coal when sampled, and which are likely to be classified on the "moist" basis, shall be marked by the sampler, equilibrated, and the analyses designated in accordance with the fifth paragraph of the section above on sampling.

<sup>94</sup> J. A. Holmes, The Sampling of Coal in the Mine, U. S. Bureau of Mines Technical Paper No. 1, 1918.

<sup>95</sup> Edgar Stansfield and K. C. Gilbert, Moisture Determination for Coal Classification, Transactions, Am. Inst. Mining and Metallurgical Engrs., Coal Division, p. 125, 1932.

**Methods of Analysis and Tests.** Laboratory Sampling and Analysis.—The coal should be prepared and analyzed in accordance with the Methods of Laboratory Sampling and Analysis of Coal and Coke (ASTM Designation: D271, p. 1145).

**Weathering or Slacking Index.**—The weathering or slacking characteristics of coals shall be determined by the U. S. Bureau of Mines method<sup>96</sup> modified with respect to the selection of a standard humidity. Briefly, the test consists of air-drying 500 to 1000 g. of approximately 1- to 1.5-in. lumps at a temperature of 30° to 35°C. and a humidity of 30 to 35% for a period of 24 hr. and then immersing the lumps in water for 1 hr., the water then being drained off, and the sample again air-dried for 24 hr. The amount of disintegration is determined by sieving on an 8-in. wire-mesh sieve with 0.263-in. square openings, and weighing the quantity of coal passing (undersize) and that retained on (oversize) the sieve. The percentage of coal passing the sieve (undersize), after deducting a blank sieving test, is the weathering or slacking index of the coal.

**Agglomerating Index.**—The coke-button grading test<sup>97</sup> afforded by the examination of the residue in the platinum crucible incident to the volatile matter determination should be used.

**Calculation to Mineral-Matter-Free Basis.** Calculation of Fixed Carbon and Btu.—For classification of coal according to rank, fixed carbon and Btu should be calculated to the mineral-matter-free basis in accordance with either the Parr formulas,<sup>98</sup> Eqs. (1), (2), and (3), or the approximation formulas, Eqs. (4), (5), and (6), given below. In case of litigation, the appropriate Parr formula should be used.

Calculation from "moist" basis:

*Parr Formulas:*

$$\text{Dry, } Mm\text{-free } FC = \frac{FC - 0.15S}{100 - (M + 1.08A + 0.55S)} \times 100 \quad (1)$$

$$\text{Dry, } Mm\text{-free } VM = 100 - \text{Dry, } Mm\text{-free } FC \quad (2)$$

$$\text{Moist, } Mm\text{-free } Btu = \frac{Btu - 50S}{100 - (1.08A + 0.55S)} \times 100 \quad (3)$$

NOTE.—The above formula for fixed carbon is derived from the Parr formula for volatile matter.

*Approximation Formulas:*

$$\text{Dry, } Mm\text{-free } FC = \frac{FC}{100 - (M + 1.1A + 0.1S)} \times 100 \quad (4)$$

$$\text{Dry, } Mm\text{-free } Vm = 100 - \text{Dry, } Mm\text{-free } FC \quad (5)$$

$$\text{Moist, } Mm\text{-free } Btu = \frac{Btu}{100 - (1.1A + 0.1S)} \times 100 \quad (6)$$

<sup>96</sup> A. C. Fieldner, W. A. Selvig, and W. H. Frederic, Accelerated Laboratory Test for Determination of Slacking Characteristics of Coal, U. S. Bureau of Mines Report of Investigations No. 3055, 1930.

<sup>97</sup> R. E. Gilmore, G. P. Connell, and J. H. H. Nicolls, Agglomerating and Agglutinating Tests for Classifying Weakly Caking Coals, Transactions, Am. Inst. Mining and Metallurgical Engrs., Coal Division, 108, p. 255, 1934.

<sup>98</sup> S. W. Parr, The Classification of Coal, Bulletin No. 180, Engineering Experiment Station University of Illinois, 1928.



where *Mm* = mineral matter,

*Btu* = British thermal units,

*FC* = percentage of fixed carbon,

*VM* = percentage of volatile matter,

*M* = percentage of moisture,

*A* = percentage of ash,

*S* = percentage of sulfur, and

Moist refers to coal containing its natural bed moisture, but not including visible water on the surface of the coal. See section on sampling, p. 1256.

**Modification for Coals High in Carbonate.**—In case of controversy, samples containing more than 1.0% of carbon dioxide occurring as carbonates shall be either (1) crushed to pass through an 840-micron (No. 20) sieve and floated on a heavy liquid of such specific gravity as to reduce the carbon dioxide occurring as carbonate to 1.0% or less on a dry basis, provided, however, that the recovery of float coal shall be not less than 75%; or (2) shall be analyzed for mineral matter according to the Parr method<sup>99</sup> for coals with high calcium carbonate content, modified by heating the sulfated ash at 750°C. to constant weight to ensure expulsion of excess sulfur trioxide.<sup>100</sup> In case of litigation, method (1) shall be used.

### SAMPLING COKE FOR ANALYSIS<sup>101</sup>

It is imperative that every sample be collected and prepared carefully and conscientiously and in strict accordance with the standard procedure described herein, for if the sampling is improperly done, the sample will be in error, and it may be impossible or impracticable to take another sample; whereas, if an analysis is in error, another analysis can readily be made of the original sample.

Gross samples of not less than the quantities designated in this method must be taken whether the coke to be sampled consists of a few tons or several hundred tons in order to minimize the effect of the chance inclusion or exclusion of too many or too few pieces of nonrepresentative material.

**Sample for All Determinations Except Total Moisture.** *Place of Sampling.*—The coke should be sampled while it is being loaded into or unloaded from railroad cars, ships, barges, or trucks, or when discharged from supply bins, railroad cars, grab buckets, or other coke-conveying equipment.

Samples collected from the surface of coke in piles, bins, cars, ships, or barges are, in general, unreliable because of size segregation and should not be used for determining conformance to specifications unless the purchaser and the seller so agree. In case it is necessary to collect a sample of coke from the surface of loaded shipments, nine equal increments should be taken about 1 ft. below the surface. The nine sampling points should be located as shown in Fig. 31-33.

**Size of Increments.**—To collect samples, a shovel or specially designed tool or mechanical means should be used for taking equal portions or increments. The

<sup>99</sup> S. W. Parr, Chemical Study of Illinois Coal, Illinois Coal Mining Investigations, State Geological Survey, Urbana, Ill., Bulletin No. 3, p. 35, 1916.

<sup>100</sup> O. W. Rees, Determining Ash in High Carbonate Coals. Study of the Modified Method, Industrial and Engineering Chemistry, Analytical Edition, 9, pp. 307-309, 1937.

<sup>101</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D346-35.

gross sample should consist of not less than 25 nor more than 50 increments of approximately equal quantity, except that when samples are collected from the surface of loaded shipments the gross sample should consist of 9 increments of approximately equal quantity.

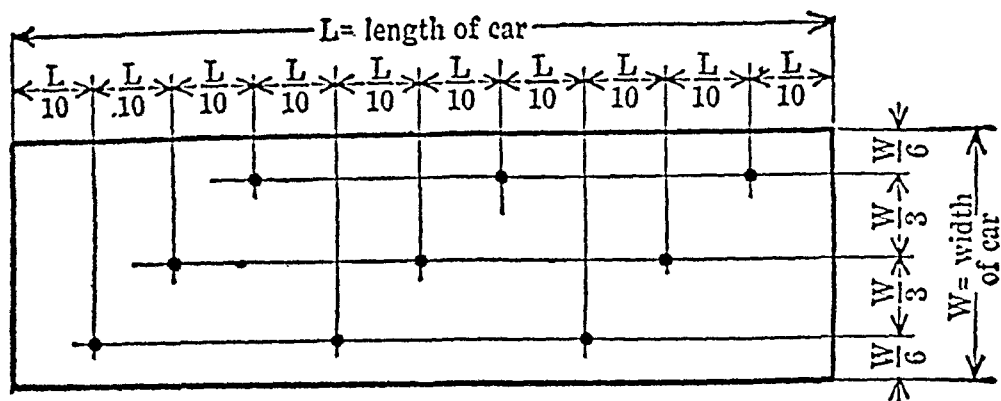


FIG. 31-33. Location of Sampling Points from Exposed Surface of Car.

**Collection of Gross Sample.**—The increments should be regularly and systematically collected, so that the entire quantity of coke sampled will be represented proportionately in the gross sample, and with such frequency that a gross sample of the required amount will be collected. The standard gross sample should be not less than the quantities given in the following table:

	<i>Minimum Weight of Gross Samples, lb.</i>
Run-of-oven, blast-furnace, foundry, water-gas, and any coke containing a range of size of pieces made from uncrushed or coarsely crushed coal, <sup>b</sup> except coke breeze . .	500 <sup>a</sup>
Run-of-oven, blast-furnace, foundry, water-gas, and any coke containing a range of size of pieces made from crushed coal, <sup>c</sup> except coke breeze . . . . .	250 <sup>a</sup>
Closely-sized coke made from uncrushed or coarsely crushed coal <sup>b</sup> free of coke breeze . . . . .	250 <sup>a</sup>
Closely-sized coke made from crushed coal <sup>c</sup> free of coke breeze . . . . .	125 <sup>a</sup>
Coke breeze (all passing a $\frac{1}{2}$ or $\frac{3}{4}$ -in. square-hole sieve) . .	125

<sup>a</sup> In case the pulverization of the coal is not known, take quantities designated for coke made from uncrushed or coarsely crushed coal.

<sup>b</sup> More than 10% on a  $\frac{1}{4}$ -in. square-hole sieve.

<sup>c</sup> Not less than 90% passing through a  $\frac{1}{4}$ -in. square-hole sieve.

**Quantity Represented.**—A gross sample should be taken for each 250 tons or fraction thereof, or in case of larger tonnages, for such quantities as may be agreed upon. Each lot of coke arising from a different source or known to be of different quality or size should be sampled separately.

**Crushing Sample.**—The entire gross sample should be crushed, mixed, and reduced in quantity to convenient size for transmission to the laboratory. The sample should be crushed preferably by means of jaw or roll crushers, or in case mechanical crushing means are not available, the coke sample should be crushed on a chilled-iron or hard-steel plate by impact of a tamper, hard bar, or sledge, avoiding all rubbing action as otherwise the ash content may be materially increased by the addition of iron from the sampling apparatus even though hardened iron or steel is used. The crushing should be done under such conditions as will prevent loss of coke or accidental admixture of foreign matter. Samples of the quantities indicated in Table 31-9 should be crushed so that no pieces of coke and impurities will be greater in dimension, as judged by eye, than specified for the sample before division into two approximately equal parts.

The method of reducing by hand the quantity of coke in a gross sample should be carried out as described in the following section, even should the initial size of coke and impurities be less than indicated in Table 31-9.

TABLE 31-9. WEIGHTS OF COKE SAMPLES WITH CORRESPONDING CRUSHING SIZES

<i>Weight of Sample to be Divided, lb.</i>	<i>Largest Size of Coke and Impurities Allowable in Sample Before Division, in.</i>
250 or over.....	1
125.....	$\frac{3}{4}$
60.....	$\frac{1}{2}$
30.....	$\frac{1}{4}$

**Mixing and Reduction.**<sup>102</sup> The progressive reduction in the weight of the sample to the quantities indicated in Table 31-9 should be done by the following methods, which are described and illustrated in Fig. 31-34.

The alternate-shovel method of reducing the gross sample should be repeated until the sample is reduced to approximately 125 lb., and care should be observed before each reduction in quantity that the sample has been crushed to the fineness specified in Table 31-9.

The crushed coke should be shoveled into a conical pile (see Fig. 31-34) by depositing each shovelful of coke on top of the preceding one, and then formed into a long pile in the following manner: The sampler should take a shovelful of coke from the conical pile and spread it out in a straight pile having a width equal to the width of the shovel and a length of 5 to 10 ft. The next shovelful should be spread directly over the top of the first shovelful, but in the opposite direction, and so on back and forth, the pile being occasionally flattened, until all the coke has been formed into one long pile. The sampler should then discard half of this pile, proceeding as follows:

Beginning on one side of the pile, at either end, and shoveling from the bottom of the pile, the sampler should take one shovelful and set it aside; advancing

<sup>102</sup> This figure was formerly part of the Standard Method of Sampling Coal for Analysis (ASTM Designation: D21) now superseded by the Standard Methods of Sampling Coals Classified According to Ash Content (ASTM Designation: D492), see p. 1137; it is included here to illustrate the alternate shovel, coning, and quartering method of reducing samples by hand.

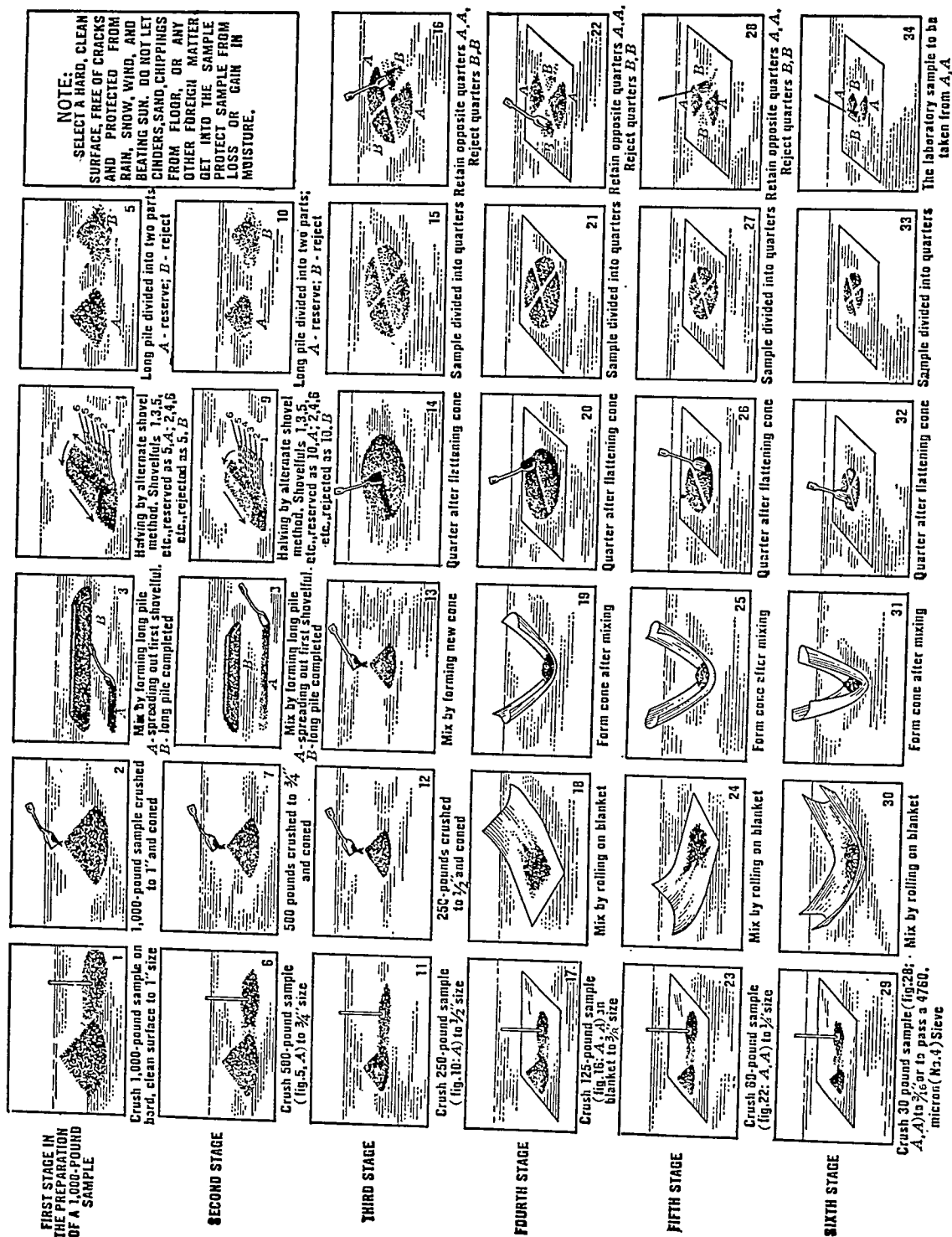


FIG. 31-34. Standard Method of Sampling Coke for Analysis.<sup>101</sup> Necessary tools: shovel, tamper, steel plate and blanket (measuring about 6 by 8 ft.). Broom, and rake. Use rake for raking over coke when crushing it, so that all lumps will be crushed. Sweep floor or blanket clean of all discarded coke after each time sample is halved or quartered.

along the side of the pile a distance equal to the width of the shovel, he should take a second shovelful and discard it; again advancing in the same direction one shovel width, he should take a third shovelful and add it to the first. The fourth should be taken in a like manner and discarded, the fifth retained, and so on, the sampler advancing always in the same direction around the pile so that its size will be gradually reduced in a uniform manner. When the pile is removed, about half of the original quantity of coke should be contained in the new pile formed by the alternate shovelfuls which have been retained.

After the gross sample has been reduced by the alternate-shovel method to approximately 125 lb., further reduction in quantity should be by the quartering method. Before each quartering, the sample should be crushed to the fineness specified in Table 31-7.

Quantities of 60 to 125 lb. should be mixed thoroughly by coning and reconing; quantities less than 60 lb. should be placed on a suitable cloth, measuring about 6 by 8 ft., mixed by raising first one end of the cloth and then the other, so as to roll the coke back and forth, and after being mixed thoroughly should be formed into a conical pile by gathering together the four corners of the cloth. The quartering of the conical pile should be done as follows:

The cone should be flattened, its apex being pressed down and worked outward by means of a shovel, so that after the pile has been quartered, each quarter will contain the material originally in it. The flattened mass, which should be of uniform thickness and diameter, should then be marked into quarters by two lines that intersect at right angles directly under a point corresponding to the apex of the original cone. The diagonally opposite quarters should then be shoveled away and discarded and the space that they occupied brushed clean. The coke remaining should be crushed, mixed, coned, and quartered successively until the sample is reduced to approximately 30 lb.

The 30-lb. quantity should be crushed to  $\frac{1}{4}$ -in. size, mixed, coned, flattened, and quartered. The laboratory samples should include all of one of the quarters, or all of the two opposite quarters, as may be required. The laboratory sample should be placed immediately in a suitable container and sealed in such a manner as to preclude tampering.

**Reduction by Mechanical Means.**—Only such riffles or other mechanical means as will give equally representative samples should be used in substitution for the hand method of reduction in quantity herein standardized.

**Sample for Determination of Total Moisture.** **Sample for Total Moisture.**—For determining total moisture, a special moisture sample weighing approximately 50 lb. should be taken, except in the case of coke breeze, in which case the moisture sample should weigh approximately 25 lb. The moisture sample should be taken when the coke is being loaded or unloaded as the case may be, and should be accumulated by placing in a waterproof receptacle with a tight-fitting lid small equal parts of the freshly-taken increments of the standard gross sample described under Size Groups (p. 1139). The special moisture sample, without any preliminary crushing, should preferably be dried to constant weight at a temperature of not less than 101° nor more than 200°C.<sup>103</sup> In case it is impracticable to dry the entire sample, the following procedures may be used:

<sup>103</sup> Experiments made at the U. S. Bureau of Mines have shown that results checking within 0.5% are obtained between these temperature limits. See A. C. Fieldner and W. A. Selvig, *The Determination of Moisture in Coke*, U. S. Bureau of Mines Technical Paper No. 148, 1917.

**For Coke Appearing Dry.**—The special moisture sample should be crushed rapidly to 0.5-in. size and reduced mechanically or by hand to about a 5-lb. quantity, which should be immediately placed in a container and sealed airtight and forwarded to the laboratory without delay.

**For Coke Appearing Wet.**—The special moisture sample should be spread on tared pans, weighed, and air-dried or dried in a warm place or on a warm or heated surface until the coke appears dry, and weighed again. The sampling should be completed as described in the preceding paragraph for coke appearing dry. This loss in weight divided by weight of sample, multiplied by 100, is the percentage of air-drying loss and should be corrected as follows for the moisture found in the sample sent to the laboratory:

$$TM = \left( \frac{100 - L}{100} \times M \right) + L$$

where  $TM$  = percentage total moisture of the coke as received,

$L$  = percentage of air-drying loss, and

$M$  = percentage moisture in the air-dried sample.

**Report.**—Since in the report of the analysis, a brief description should be given of the method of taking the sample, by such characteristic expressions as “belt sample,” “top-of-car,” etc., information as to how the sample is taken should be included in the description which accompanies the sample sent to the laboratory.

## VOLUME OF CELL SPACE OF LUMP COKE <sup>104</sup>

The percentage by volume of cell space of lump coke shall be calculated from the apparent specific gravity of the moisture-free lump coke and the true specific gravity of moisture-free coke passing a 74-micron (No. 200) sieve, as follows:

$$\text{Cell space, \% by volume} = 100 - 100 \left( \frac{\text{apparent sp. gr.}}{\text{true sp. gr.}} \right)$$

## APPARENT SPECIFIC GRAVITY

**Apparatus.**—The apparatus for the determination of the apparent specific gravity of coke consists of the following:

(a) A suitable container not smaller than approximately 13 in. in height, 22 in. in length, and 11 in. in width, or of equivalent size, provided with a spout consisting of a short 0.5-in. nipple extending horizontally from the container about 2.5 in. below the top.

**NOTE.**—A wash boiler of suitable size to which a spout has been soldered answers the above description.

(b) A wire cage or basket of about 0.5-in. square-mesh screen wire cloth provided with a cover and two long handles, suitable for holding the entire sample of coke and so made as to fit inside the container below the spout.

(c) A 3-gallon bucket or other vessel suitable for receiving the displaced water.

(d) A pan about 15 in. square and 3 in. in height or the equivalent for containing the coke during the determination of its weight.

<sup>104</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D167-24.

(e) A scale sensitive to 0.5 oz.

**Sampling. Unit for Sampling.**—Each carload or its equivalent should be considered a unit for sampling.

**Sampling at Source.**—If the porosity test is desired on run-of-oven coke, the sample should be collected from the coke wharf in the case of by-product coke, while samples of beehive coke should be collected as the coke is drawn from the ovens.

**By-Product Coke.**—About 50 lb. of representative pieces of coke should be selected from the coke wharf for each test. This is best accomplished by dividing the coke on the wharf into approximately equal areas and selecting an equal number of pieces from each area. Each piece selected should be approximately equal in length to one-half of the width of the coke ovens, and should show a "cauliflower" end produced at the walls of the ovens, and an "inner" end produced at the center of the ovens.

**Beehive Coke.**—About 50 lb. of representative pieces of coke should be selected for each test as the coke is drawn from the ovens. This is best done by selecting full-length pieces, or their equivalent, as the coke is being drawn from previously determined points in the oven, so that they include pieces from the front, sides, center, and back. If the individual pieces as taken from the ovens are too large and bulky, the 50-lb. sample should be collected by removing three small pieces from each large piece—one each from the top, the middle, and the bottom. The sample finally collected should be composed of an equal number of pieces showing top, middle, and bottom.

**Sampling at Delivery.**—If the porosity test is desired on coke for furnace or cupola use, the sample should be representative of the material in question and collected at the place of delivery.

**By-Product and Beehive Coke.**—The sample is best collected as the coke is delivered from the railroad cars into the bins. This may be accomplished by inserting a scoop of 10- to 15-lb. capacity in the coke stream at regular intervals during the period of unloading. The sample collected should be large enough to give about 50 lb. of coke pieces, none of which would in any position pass through a 1-in. square-mesh sieve.

**NOTE.**—Since the cage or basket is of 0.5-in. square-mesh screen wire cloth, it is necessary to have pieces that will remain in the cage when it is removed from the water.

As it is very difficult to collect a representative sample from coke exposed in bins and cars, care should be taken to take pieces representing the entire exposed area, if sampling must be done in this manner. This is best accomplished by dividing the exposed surface to be sampled into approximately equal areas, and selecting an equal number of pieces from each area. A 50-lb. sample of representative pieces should be collected, none of which should in any position pass through a 1-in. square-mesh sieve.

**Procedure.**—Select about 25 lb. of coke from the sample so that it is representative of the material under consideration with regard to size, shape, and general appearance. Dry the coke to constant weight at a temperature of from 105° to 200°C. Weigh the coke when cool, after shaking and brushing off any adhering dust.

Place a cork in the spout of the container, which has been placed on a level and rigid base or floor. After the empty cage has been placed into the container, pour water at room temperature into the container until the water level is above

the spout. After the water has come to rest, remove the cork from the spout and permit the excess water to drain out for 1 minute after the overflow stream starts to discharge drop by drop. Then replace the cork and remove the cage from the water, care being taken to shake all adhering water back into the container. Then place the weighed dried coke sample into the cage and after fastening the cover, lower the cage containing the coke into the water.

NOTE.—If there is not sufficient capacity in the container above the spout to retain the displaced water, some of the water may be drawn off into a weighed bucket, or other suitable vessel, by removing the cork from the spout while the coke is being lowered.

Permit the cage to remain in the water for 15 minutes, with occasional shaking to detach any air bubbles adhering to the surface of the coke, care being taken not disturb the position of the container. At the end of the 15-minute period, during which the coke shall have been completely submerged at all times, remove the cork after the water has come to rest, and permit the displaced water to drain into a weighed bucket or other suitable vessel for 1 minute after the overflow stream starts to discharge drop by drop. Replace the cork, remove the cage containing the coke from the water and permit it to drain for 1 minute. Remove the wet coke from the cage and weigh it.

Determine the weight of the displaced water, which has been caught in the bucket.

Calculation.—The apparent specific gravity shall be calculated from the formula:

$$\text{Apparent specific gravity} = \frac{A}{B + (C - A)}$$

where  $A$  = weight of dry coke,

$B$  = weight of water displaced by wet coke, and

$C$  = weight of wet coke.

### TRUE SPECIFIC GRAVITY

*Apparatus.*—The apparatus for the determination of the true specific gravity of coke passing a 74-micron (No. 200) sieve shall consist of a Hogarth's specific gravity bottle with side tubulure, having a capacity of about 100 ml. The bottle should be accurately calibrated so that a table may be constructed giving the contents of the bottle at the room temperatures likely to occur in the laboratory.

NOTE.—This may be done conveniently from data in tables of corrections for determining the true capacities of glass vessels from the weight of water in air, as given in National Bureau of Standards Circular No. 19, pp. 52–56, 1916.

*Procedure.*—Carefully introduce a 10-g. portion of 200-mesh coke which has been previously dried for 1 hr. at 105°C., into the specific gravity bottle with a sufficient quantity of distilled water to fill the bottle about one-half full. Then place the bottle on a hot plate and keep the contents boiling for 1 hr., the specific gravity bottle being shaken frequently so as to wash down any coke adhering to the sides. Remove the bottle from the plate, after boiling for 1 hr., fill it to the tubulure with recently boiled and cooled distilled water, and insert the stopper. Permit the bottle to stand until the contents have cooled to room temperature (see Note 1, below), then fill the bottle to slightly above the mark on the capillary of the stopper with recently boiled distilled water which has been cooled to room temperature (see Note 2, below). Adjust the water level to the mark on the capillary by touching a piece of filter paper to the end of the tubulure. Then wipe the bottle



dry and weigh it immediately. Immediately after the weighing, remove the stopper and take the temperature of the contents.

NOTE 1.—Cooling may be hastened by placing the bottle in water.

NOTE 2.—This is conveniently done by inserting the end of the tubulure in a small beaker of the distilled water and applying a slight suction on the stopper.

**Calculation.**—The true specific gravity shall be calculated from the formula:

$$\text{True specific gravity} = \frac{W}{W - (W' - P)}$$

where  $W$  = weight in grams of dry coke,

$W'$  = weight in grams of the bottle and the dry coke and water required to fill it,

$P$  = weight in grams of the bottle and the water required to fill it.

**Reproducibility of Results.**—The differences in duplicate determinations of true specific gravity shall not be more than the following:

Same analysts.....	0.01
Different analysts.....	0.02

### DROP SHATTER TEST FOR COKE <sup>105</sup>

This method of drop shatter test is intended for determining the property of coke to withstand breakage when subjected to handling at the source and during transit to the consumer.

**Apparatus. Shatter Test Machine.**—The shatter test machine consists of a box 18 in. in width, 28 in. in length, and approximately 15 in. in depth, supported above a rigidly mounted cast-iron or steel plate, not less than 0.5 in. in thickness, 38 in. in width, and 48 in. in length. The inside of the bottom of the box should be 6 ft. above the plate. The bottom of the box should consist of two doors hinged lengthwise and latched so that they will swing open freely and not impede the fall of the coke. Boards about 8 in. in height should be placed around the plate so that no coke is lost. To prevent the breakage of coke, which may occur while placing the sample in the box, the box should be constructed so that it can be lowered to a convenient level, which is best done by means of a pulley and counter-weight. A convenient form of shatter test machine is shown in Fig. 31-35.

**Sieves.**—For determining the breakage of coke, square-mesh sieves of the following sizes should be used: 2, 1.5, 1, and 0.5-in. The sieves shall conform to the Specifications for Sieves for Testing Purposes (ASTM Designation: E11, p. 1277), except that circular sieves 2 ft. in diameter are satisfactory.

**Sampling. Unit for Sampling.**—Each carload or its equivalent should be considered a unit for sampling.

**Sampling at Source.**—If the shatter test is to be used to indicate the probable breakage of coke on handling, the sample should be taken before the coke is subjected to possible breakage resulting from screening and loading into cars. In the case of by-product coke, the sample should be collected from the coke wharf; samples of beehive coke should be collected as the coke is drawn from the ovens.

**By-Product Coke.**—About 75 lb. of representative pieces of coke, none of which would in any position pass through a 2-in. square-mesh sieve, should be selected

<sup>105</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM, Committee D-5 on Coal and Coke. Standardized as D141-48.

from the coke wharf for each test. This is best accomplished by dividing the coke on the wharf into approximately equal areas and selecting an equal number of pieces from each area. Each piece selected should be approximately equal in

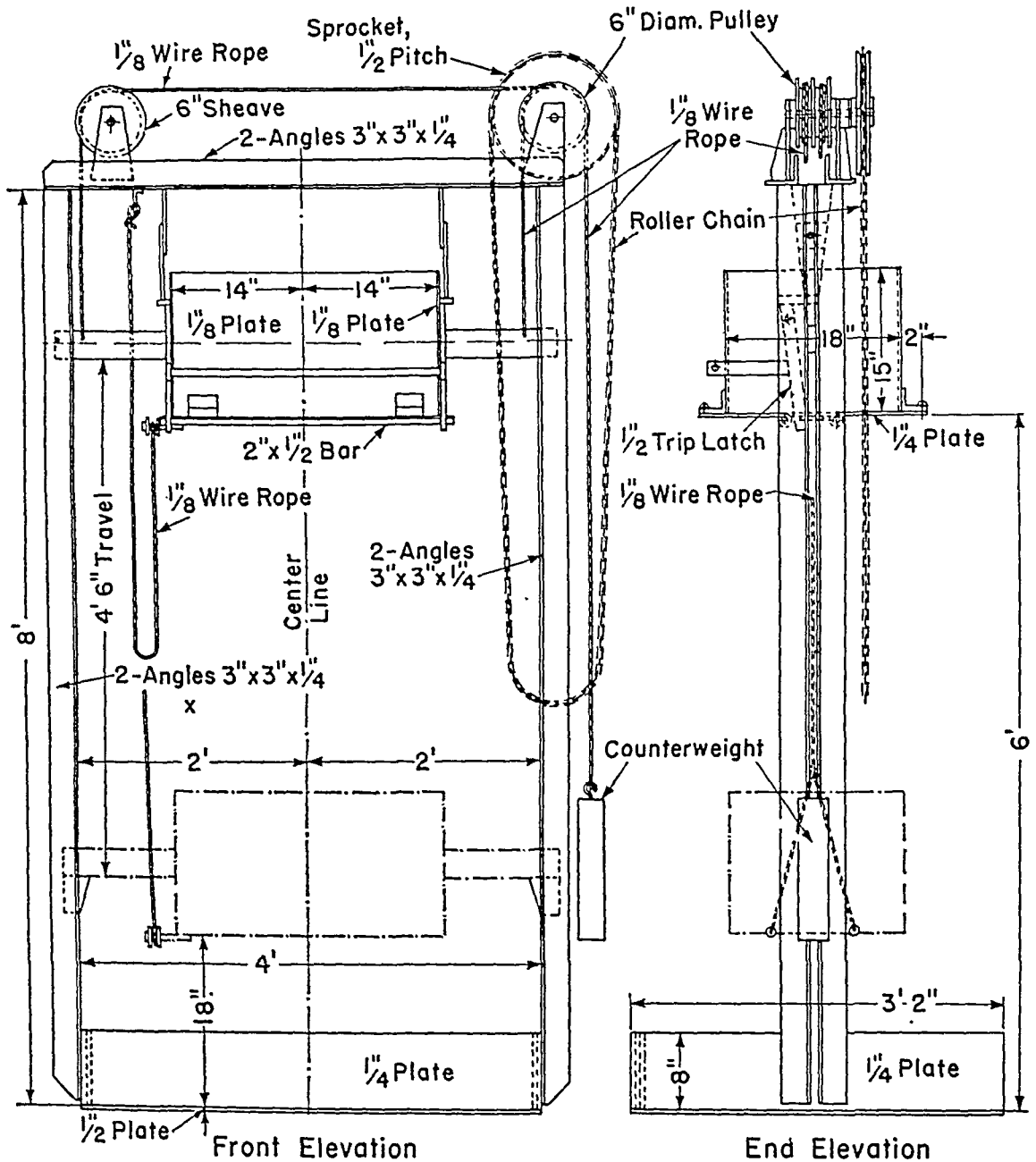


FIG. 31-35. Shatter Test Machine.

length to one-half the width of the coke-ovens, and shall show a "cauliflower" end produced at the walls of the ovens and an "inner" end produced at the center of the ovens.

**Beehive Coke.**—About 75 lb. of representative pieces of coke should be selected for each test as the coke is drawn from the ovens. This is best done by selecting full-length pieces or their equivalent as the coke is being drawn from previously

determined points in the oven, so that they include pieces from the front, sides, center, and back. If the individual pieces as taken from the ovens are too large and bulky, the 75-lb. sample should be collected by removing three small pieces from each large piece—one each from the top, the middle, and the bottom. The sample finally collected should be composed of an equal number of pieces showing top, middle, and bottom. None of the pieces comprising the sample should in any position pass through the 2-in. square-mesh sieve.

**Sampling at Delivery.**—If the shatter test is to be used to indicate the fitness of the coke for furnace or cupola use, the sample should be collected at the place of delivery.

**By-Product and Beehive Coke.**—The sample is best collected as the coke is delivered from the railroad cars into the bins. This may be accomplished by inserting a scoop of 10- to 15-lb. capacity in the coke stream at regular intervals during the period of unloading. The sample collected should be large enough to give about 75 lb. of coke pieces, none of which would in any position pass through a 2-in. square-mesh sieve.

As it is very difficult to collect a representative sample from coke exposed in bins and cars, care should be taken to take pieces representing the entire exposed area, if sampling must be done in this manner. This is best accomplished by dividing the exposed surface to be sampled into approximately equal areas, and selecting an equal number of pieces from each area. A 75-lb. sample of representative pieces should be collected, none of which shall in any position pass through a 2-in. square-mesh sieve.

**Procedure.**—Place about 50 lb. of the sample in the box of the coke shatter test machine, level the coke, raise the box, and drop the coke four times on the plate, the small material produced being returned each time to the box with the large coke. To prevent breakage of the coke, lower the box to a convenient height when transferring the sample into it. After the fourth drop, run the material successively through the 2-in., 1.5-in., 1-in., and 0.5-in. sieves. The coke should be sieved in such increments as will allow all pieces to be in direct contact with the sieve openings.

In sieving, care should be taken to prevent breakage of the coke pieces. Shake the sieve gently until all of the pieces are in direct contact with the meshes. Weigh the coke remaining on each sieve and that which passes through separately. If the sum of these weights shows a loss of over 1%, reject the test and make another test.

**Report.**—The results of the shatter test should be reported as follows:

<i>Passing</i>	<i>Retained on</i>	<i>Per Cent</i>
	2-in. sieve.....	
2-in. sieve	1.5-in. sieve.....	
1.5-in. sieve	1-in. sieve.....	
1-in. sieve	0.5-in. sieve.....	
0.5-in. sieve	.....	

Since the average probable error of a single shatter test determination is approximately 2%, it is advisable to make several tests and report the average result.

TUMBLER TEST FOR COKE<sup>106</sup>

This tumbler test is a relative measure of the resistance of the coke to degradation by abrasion. The results obtained are influenced by the effect of impact.

**Apparatus. Tumbler Machine.**—The tumbler machine consists of a circular steel drum 36 in. in inside diameter and 18 in. in inside length made of plate at least  $\frac{1}{4}$  in. in thickness. Two equally spaced 2 by 2 by  $\frac{1}{4}$ -in. angles should be riveted longitudinally inside the drum. These angles should be riveted to the shell so that the attached legs point away from the direction of rotation, thus giving a clear unobstructed shelf for lifting the coke. To provide for rotating the drum, it should be mounted on a horizontal steel shaft 1.5 in. in diameter passing through the drum. An opening should be provided, preferably in the shell, for introducing and removing the sample. During the test, the cover should be rigidly fastened to the shell and shall be so constructed as to fit into the shell in order to have a smooth inner surface.

**Sieves.**<sup>107</sup>—For sizing the sample for test, square-mesh sieves having 2-in. and 3-in. actual openings between the wires should be used. For sieving the coke after the tumbler test, square-mesh sieves having 2, 1.5, 1, 0.5, and  $\frac{1}{4}$ -in. actual openings between the wires should be used. The sieves shall conform to the Specifications for Sieves for Testing Purposes (ASTM Designation: E11, p. 1277), except that sieves of heavy double-crimped wire with circular frames about 24 in. in diameter are satisfactory.

**Sampling.**—The gross sample collected should be sufficient to obtain approximately 25 lb. of coke which will pass a 3-in. sieve and be retained on a 2-in. square-mesh sieve. This may be best accomplished by placing a container or scoop in the stream of coke and collecting small increments at regular intervals in order to obtain a representative sample of the entire quantity of coke under consideration.

**Preparation of Sample.**—Size the coke by sieving on 3-in. and 2-in. square-mesh sieves, without crushing the larger pieces, in order to obtain a sample that will pass the 3-in. sieve and be retained on the 2-in. sieve. In sizing the sample, up-end each piece of coke on the sieve by hand to determine whether in any position it passes the sieve. If a large proportion of the pieces are larger than 3 in. it will be necessary to break out representative smaller pieces of the desired size. This should be accomplished without shattering the coke pieces and may often be done with a heavy screw driver by prying apart at fracture cracks.

**Procedure.**—Accurately weigh approximately 22 lb. (10 kg.) of the coke sample which has been sized in accordance with the preceding section, and previously dried at 104° to 200°C., and place it in the drum of the tumbler machine. Rigidly fasten the cover and rotate the drum at  $24 \pm 1$  r.p.m. for a total of 1400 revolutions. Then remove all of the coke from the drum and sieve it, using the following square-mesh sieves: 2, 1.5, 1, 0.5, and  $\frac{1}{4}$ -in. Up-end each piece of coke retained on the 2-in. sieve by hand to determine whether in any position it passes the 2-in. sieve. Shake the coke passing the 2-in. sieve rather vigorously on each succeeding sieve

<sup>106</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D294-50.

<sup>107</sup> User's attention is called to the fact that yields of certain sizes as determined by use of the specified screens cannot be compared directly with results obtained by using screens as specified prior to the 1950 revision. An important example occurs in the case of the tumbler test stability factor (per cent remaining on 1 in. after tumbling) which will be slightly higher than comparable previous results using the formerly specified 1.06-in. screen.

in order to up-end the pieces until practically no more coke will pass through the openings. Weigh separately the coke retained on each sieve and that which passes through the smallest sieve used. Make the weighings to the nearest 1 g.

**Report.**—The sieve analysis after the tumbler test shall be reported in cumulative percentages to the nearest 0.1%, as follows:

<i>Total Retained On</i>	<i>Per Cent, Cumulative</i>
2-in. sieve . . . . .	
1.5-in. sieve . . . . .	
1-in. sieve . . . . .	(Stability Factor) *
0.5-in. sieve . . . . .	
$\frac{1}{4}$ -in. sieve . . . . .	(Hardness Factor) *

\* The percentage of coke retained on the 1-in. sieve has been designated the stability factor and the percentage retained on the  $\frac{1}{4}$ -in. sieve as the hardness factor as indicated in the report of the sieve test in the above table.

### SIEVE ANALYSIS OF COKE <sup>108</sup>

**Sieves.**—Square-hole sieves of the following sieve openings <sup>109</sup> conforming to the Tentative Specifications for Sieves for Testing Purposes (ASTM Designation: E11, p. 1277) should be used:

<i>Size</i>	<i>Sieve Opening, in.</i>
3360 micron (No. 6) . . . . .	0.132
4760 micron (No. 4) . . . . .	0.187
$\frac{1}{4}$ in. . . . .	0.250
$\frac{3}{8}$ in. . . . .	0.375
$\frac{1}{2}$ in. . . . .	0.500
$\frac{3}{4}$ in. . . . .	0.750
1 in. . . . .	1.00
1 $\frac{1}{2}$ in. . . . .	1.50
2 in. . . . .	2.00
3 in. . . . .	3.00
4 in. . . . .	4.00

For sizes of coke smaller than 2 in., sieves of double-crimped wire with circular frames about 18 in. in diameter are satisfactory. For coke 2 in. and larger in size, it is more convenient to use sieves square or rectangular in shape of heavy, double-crimped wire, having an area of 6 to 9 sq. ft. These larger sieves may be mounted so as to slide like drawers, in a rack, with a pan at the bottom.

**Sampling.**—For collecting samples of coke, the procedure described in the relevant sections of the Standard Methods of Sampling Coals Classed According to Ash Content (ASTM Designation: D192, p. 1137) should apply in general. The weight of the sample selected for the sieve analysis determination depends upon the size and character of the coke and shall conform to the following:

<sup>108</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as D293-50.

<sup>109</sup> User's attention is called to the fact that yields of certain sizes as determined by use of the specified screens cannot be compared directly with results obtained by using screens as specified prior to the 1950 revision.

*Minimum Weight  
of Sample, lb.*

For run-of-oven coke and coke 1 in. and larger in size containing breeze.....	500
For coke 1 in. and larger in size, free from breeze....	200
For coke smaller than 1 in. in size.....	50

It is extremely difficult to obtain truly representative samples of coke having a range of sizes. When the coke is on a belt conveyor the sample should be selected by stopping the belt at regular intervals and selecting increments in sections about 3 ft. in length and the entire width of the belt, or when the coke is going over a pulley or coming down a chute the sample should be selected by inserting a container or scoop into the stream of coke at regular intervals so as to take increments of the full width and thickness. The increments should be regularly and systematically collected so that the entire quantity of coke sampled will be represented proportionately in the sample, and with such frequency that a sample of the required amount is collected. It is not feasible to collect representative samples of coke from loaded cars or bins for sieve analyses. Samples of coke in cars or bins should be taken as the cars or bins are being filled or emptied.

*Procedure.*—The sample should be accurately weighed. Starting with the sieve having the largest opening, the sample of coke should be sieved in such increments as will allow the pieces to be in direct contact with the meshes after the completion of the shaking of each increment. For coke 1 in. and larger in size the following square-mesh sieves are usually used: 4, 3, 2, 1.5, 1, and 0.5 in. For coke smaller than 1 in. in size the square-mesh sieves usually used are:  $\frac{3}{4}$ ,  $\frac{1}{2}$ ,  $\frac{3}{8}$ ,  $\frac{1}{4}$ , 0.187, and 0.132 in. Each piece of coke retained on the 2-in. or larger sieve should be up-ended by hand on the sieve, to determine whether in any position it passes through the sieve. Coke pieces passing the 2-in. sieve should be shaken rather vigorously on each succeeding sieve in order to up-end the pieces until practically no more coke will pass through the openings. The coke retained on each sieve and that which passes the smallest sieve used should be weighed separately. In case the coke is wet, it should be dried before making the sieve analysis. However, any error due to moisture content would usually be very small and may be neglected except in the case of coke smaller than 1 in. in size, in which case the coke should be dried before making the sieve test.

*Report.*—The sieve analysis of the coke should be reported in percentage to the nearest 0.1% as follows:

<i>Passing</i>	<i>Retained on</i>	<i>Per Cent</i>
	4-in. sieve.....	
4-in. sieve	3-in. sieve.....	
3-in. sieve	2-in. sieve.....	
2-in. sieve	1.5-in. sieve.....	
1.5-in. sieve	1-in. sieve.....	
.....	.....	
.....	.....	
0.187-in. sieve	0.132-in. sieve.....	
0.132-in. sieve.....	.....	
Total.....		100.0

In case the sum of the percentages does not total 100.0, correction should be made on the quantity passing through the smallest sieve so that the total will be 100.0. However, if the sum of the weights retained on each sieve and that which passes the smallest sieve shows a loss of over 0.5%, the analysis should be rejected and another test made.

In view of the difficulty of obtaining representative samples of coke with regard to the size of pieces, even when 500-lb. samples are used for the sieve analysis, it is desirable to take several samples for sieve tests and average the figures for the several samples.

### CUBIC FOOT WEIGHT OF COKE <sup>110</sup>

This method of test covers a procedure for determining the cubic foot weight of coke 5 in. and smaller, that is, coke which would in any position pass through a 5-in. square-mesh sieve.

**Measuring Box.**—A box 24 by 24 by 24 in. in inside dimensions should be used. In order to keep it as light in weight as possible, the box may be made of wood, but it must be rigid. Two strips of wood may be fastened to the sides of the box to form "sedan-chair" handles for convenience in handling.

**NOTE.**—For determining the cubic foot weight of coke smaller than 1 in. in size, a measuring box 12 by 12 by 12 in. in inside dimensions may be used.

**Sampling.**—For collecting samples of coke, the procedure described in the relevant sections of the Methods of Sampling Coals Classed According to Ash Content (ASTM Designation: D492, p. 1137) should apply in general. The weight of the sample selected for the determination of the cubic foot weight depends upon the size and character of the coke and shall conform to the following:

For run-of-oven coke and coke 1 in. up to 5 in. in size. . . . not less than 300 lb.

For coke smaller than 1 in. in size. . . . . not less than 50 lb.

It is extremely difficult to obtain truly representative samples of coke having a range of sizes. When the coke is on a belt conveyor the sample should be selected by stopping the belt at regular intervals and selecting increments in sections about 3 ft. in length and the entire width of the belt, or when the coke is going over a pulley or coming down a chute the sample should be selected by inserting a container or scoop into the stream of coke at regular intervals so as to take increments of the full width and thickness. The increments should be regularly and systematically collected, so that the entire quantity of coke sampled will be represented proportionately in the sample, and with such frequency that a sample of the required amount should be collected. It is not feasible to collect representative samples of coke from loaded cars or bins for cubic foot weight determinations. Samples of coke in cars or bins should be taken as the cars or bins are being filled or emptied.

**Procedure.**—The measuring box should be placed on a suitable platform scale, weighed empty, and then filled with coke from the sample while the box is on the scale in order to avoid handling the heavy box of coke. The box should be filled by means of a shovel or other suitable container by allowing the coke to slide out

<sup>110</sup> Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D292-59

of the shovel or container from a height of 2 in. above the top of the box, with no attempt to spread or arrange the coke. Because of the physical character of coke it is not practical to strike off the excess coke by means of a straight-edge, so it is necessary to do this largely by eye with the assistance of a straight-edge to check observations. The box should not be shaken, tapped, or dropped during filling or leveling off. The box filled with coke should then be weighed. The difference between the two weights divided by the number of cubic feet in the box will give the weight per cubic foot of coke.

**NOTE.**—For proper interpretation of the cubic foot weight of coke, a moisture determination and a sieve analysis of the coke should be reported along with the cubic foot weight. For directions for making these determinations see the following methods:

**Moisture.**—Methods of Laboratory Sampling and Analysis of Coal and Coke (ASTM Designation: D271, p. 1145).

**Sieve Analysis.**—Method of Test for Sieve Analysis of Coke (ASTM Designation: D293, p. 1272).

## TERMS RELATING TO COAL AND COKE <sup>111</sup>

**Proximate Analysis.**—In the case of coal and coke, the determination, by prescribed methods, of moisture, volatile matter, fixed carbon (by difference), and ash.

**NOTE.**—Unless otherwise specified, the term “proximate analysis” does not include determinations of sulfur or phosphorus or any determinations other than those named.

**Ultimate Analysis.**—In the case of coal and coke, the determination of carbon and hydrogen in the material, as found in the gaseous products of its complete combustion, the determination of sulfur, nitrogen, and ash in the material as a whole, and the estimation of oxygen by difference.

**NOTES.**—The determination of phosphorus is not by definition a part of the ultimate analysis of coal or coke, but may be specified when desired.

When the analysis is made on an undried sample, part of the hydrogen and oxygen as determined is present in the free moisture accompanying the coal. Therefore, in comparing coals on the basis of their ultimate analysis, it is advisable always to state the analysis on both the “as-received” and “dry” bases.

Inasmuch as some coals contain mineral carbonates, and practically all contain clay or shale containing combined water, a part of the carbon, hydrogen, and oxygen found in the products of combustion may arise from these mineral components.

**Moisture.**—Essentially water, quantitatively determined by definite prescribed methods which may vary according to the nature of the material.

**NOTES.**—Such methods may not determine all of the water present.

In the case of coal and coke the methods employed shall be those prescribed in the Methods of Laboratory Sampling and Analysis of Coal and Coke (ASTM Designation: D271, p. 1150).

**Ash.**—Inorganic residue remaining after ignition of combustible substances, determined by definite prescribed methods.

**NOTES.**—Ash may not be identical, in composition or quantity, with the inorganic substances present in the material before ignition.

In the case of coal and coke, the methods employed shall be those prescribed in the Methods of Laboratory Sampling and Analysis of Coal and Coke (ASTM Designation: D271, p. 1151).

<sup>111</sup> Under the standardization procedure of the Society, these definitions are under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D121-30.



**Volatile Matter.**—Those products, exclusive of moisture, given off by a material as gas or vapor, determined by definite prescribed methods which may vary according to the nature of the material.

**NOTE.**—In the case of coal and coke, the methods employed shall be those prescribed in the Methods of Laboratory Sampling and Analysis of Coal and Coke (ASTM Designation: D271, p. 1152).

**Fixed Carbon.**—In the case of coal, coke, and bituminous materials, the solid residue other than ash, obtained by destructive distillation, determined by definite prescribed methods.

**NOTES.**—It is made up principally of carbon, but may contain appreciable amounts of sulfur, hydrogen, nitrogen, and oxygen.

In the case of coal and coke, the methods employed shall be those prescribed in the Methods of Laboratory Sampling and Analysis of Coal and Coke (ASTM Designation: D271, p. 1155).

**Beehive Coke.**—Coke manufactured in beehive, rectangular, or similar forms of ovens in a horizontal bed, where heat for the coking process is secured by combustion within the oven chamber.

**By-Product Coke.**—Coke manufactured with attendant recovery of by-products, in ovens that are heated externally.

**Coke Breeze.**—The fine screenings from crushed coke or from coke as taken from the ovens, of a size varied in local practice but usually passing a  $\frac{1}{2}$ -in. or  $\frac{3}{4}$ -in. screen opening.

**Dry Coke.**—A laboratory term applied to coke which has been dried to constant weight in accordance with definite prescribed methods.

**NOTE.**—The methods employed shall be those for the determination of moisture prescribed in the Methods of Laboratory Sampling and Analysis of Coal and Coke (ASTM Designation: D271, p. 1150). In the case of lump coke, the temperature shall be not less than 104°C., nor more than 200°C.; in the case of coke passing a 250-micron (No. 60) sieve, the temperature shall be not less than 104°C. nor more than 110°C. for a period of 1 hr.

**Equilibrium Moisture of Coal.**<sup>112</sup>—The moisture content retained at equilibrium in an atmosphere over a saturated solution of potassium sulfate at 30°C., and 96 to 97% relative humidity. When the sample, before such equilibration, contains total moisture at or above the equilibrium moisture, the equilibrium moisture may be considered as equivalent to *inherent* or *bed* moisture; and any excess may be considered as *extraneous* moisture.

**Gross Calorific Value (Gross Heat of Combustion),  $H_g$ .**<sup>113</sup>—In the case of solid fuels and liquid fuels of low volatility, the heat produced by combustion of unit quantity, at constant volume, in an oxygen bomb calorimeter under specified conditions.

**NOTE.**—The conditions are initial oxygen pressure of 20 to 40 atmospheres, final temperature of 68° to 95°F. (20° to 35°C.), products in form of ash, liquid water, and gaseous CO<sub>2</sub>, SO<sub>2</sub>, and nitrogen. This definition is not applied to gaseous or highly volatile liquid fuels.

<sup>112</sup> This "tentative revision" of this standard has been accepted by the Society for the purpose of eliciting criticisms of which due cognizance will be taken before the revision is approved for incorporation in the standard. Criticisms should be addressed to the Society, 1916 Race St., Philadelphia 3, Pa.

<sup>113</sup> Under the standardization procedure of the Society, these definitions are under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D407-44.

**Net Calorific Value (Net Heat of Combustion),  $H_f$ .<sup>113</sup>**—In the case of solid fuels and liquid fuels of low volatility, a lower value calculated from the gross calorific value as the heat produced by combustion of unit quantity, at constant atmospheric pressure, under conditions, such that all water in the products remains in the form of vapor.

**NOTE.**—The net calorific value (net heat of combustion) is calculated from the gross calorific value (gross heat of combustion) at 68°F. (20°C.) by making a deduction of 1030 Btu. per lb. (572 cal. per g.) of water derived from unit quantity of fuel, including both the water originally present as moisture and that formed by combustion. The deduction is not equal to the latent heat of vaporization of water (1055 Btu. per lb. at 68°F. (20°C.)) because the calculation is made to reduce from gross value at constant volume to net value at constant pressure, for which the appropriate factor under these conditions is 1030 Btu. per lb.

**Common Banded Coal.**<sup>114</sup>—The common variety of bituminous and subbituminous coal. It consists of a sequence of irregularly alternating layers or lenses of (1) homogeneous black material having a brilliant vitreous luster, (2) grayish-black, less brilliant, striated material usually of silky luster, and (3) generally thinner bands or lenses of soft, powdery, and fibrous particles of mineral charcoal. The difference in luster of the bands is greater in bituminous than in subbituminous coal.

**Splint Coal.**<sup>114</sup>—A variety of bituminous or subbituminous coal, commonly having a dull luster and grayish-black color, of compact structure, often containing a few thin irregular bands with vitreous luster. When struck, it is resonant. It is hard and tough and breaks with an irregular, rough, sometimes splintery fracture. It is free burning and does not swell on heating.

**Cannel Coal.**<sup>114</sup>—A variety of bituminous or subbituminous coal of uniform and compact fine-grained texture with a general absence of banded structure. It is dark gray to black in color, has a greasy luster, and is noticeably of conchoidal or shell-like fracture. It is noncaking, yields a high percentage of volatile matter, ignites easily, and burns with a luminous, smoky flame.

**Boghead Coal.**<sup>114</sup>—A variety of bituminous or subbituminous coal resembling cannel coal in appearance and behavior during combustion. It is characterized by a high percentage of algal remains and volatile matter. Upon distillation it gives exceptionally high yields of tar and oil.

## SIEVES FOR TESTING PURPOSES <sup>115</sup>

**Scope.**—These specifications cover wire cloth sieves, round-hole plate screens (sieves), and square-hole plate screens (sieves) for precision testing in the classification of materials according to size (mechanical analysis, fineness, and particle size determinations). The sieves covered by these specifications are intended for general precision testing (see Note, p. 1278). A method of calibrating wire cloth sieves is included as information in the Appendix, 1961 Book of ASTM Standards, Part 8, pages 1818–1823.

<sup>114</sup> Under the standardization procedure of the Society, these definitions are under the jurisdiction of the ASTM Committee D-5 on Coal and Coke. Standardized as ASTM D493-39.

<sup>115</sup> Under the standardization procedure of the Society, these specifications are under the jurisdiction of the ASTM Committee E-1 on Methods of Testing. Adopted as ASTM E11-61T.

**TABLE 31-10. NOMINAL DIMENSIONS, PERMISSIBLE VARIATIONS, AND  
LIMITS FOR WIRE CLOTH OF STANDARD SIEVES  
[U. S. Standard Series (4th Root of 2 Ratio)]**

Sieve Designation		Sieve Opening		Permissible Variations in Average Opening, per cent	Permissible Variation for not more than 5 per cent of Openings, per cent	Permissible Maximum Variation in Individual Openings, per cent	Nominal Wire Diameter <sup>b</sup>	
Standard	Alternate	mm.	in. (ap- proximate equiv- alents)				mm.	in. (ap- proximate equiv- alents)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
107.6 mm.....	4.24 in.	107.6	4.24	±3	+4	+5	6.40	0.2520
101.6 mm.....	4 in. <sup>a</sup>	101.6	4.00	±3	+4	+5	6.30	0.2480
90.5 mm.....	3½ in.	90.5	3.50	±3	+4	+5	6.08	0.2394
76.1 mm.....	3 in.	76.1	3.00	±3	+4	+5	5.80	0.2283
64.0 mm.....	2½ in.	64.0	2.50	±3	+4	+5	5.50	0.2165
53.8 mm.....	2.12 in.	53.8	2.12	±3	+4	+5	5.15	0.2028
50.8 mm.....	2 in. <sup>a</sup>	50.8	2.00	±3	+4	+5	5.05	0.1988
45.3 mm.....	1¾ in.	45.3	1.75	±3	+4	+5	4.85	0.1909
38.1 mm.....	1½ in.	38.1	1.50	±3	+4	+5	4.59	0.1807
32.0 mm.....	1¼ in.	32.0	1.25	±3	+4	+5	4.23	0.1665
26.9 mm.....	1.06 in.	26.9	1.06	±3	+5	+6	3.90	0.1535
25.4 mm.....	1 in. <sup>a</sup>	25.4	1.00	±3	+5	+6	3.80	0.1496
22.6 mm.*....	⅞ in.	22.6	0.875	±3	+5	+6	3.50	0.1378
19.0 mm.....	¾ in.	19.0	0.750	±3	+5	+6	3.30	0.1299
16.0 mm.*....	⅝ in.	16.0	0.625	±3	+5	+6	3.00	0.1181
13.5 mm.....	0.530 in.	13.5	0.530	±3	+5	+6	2.75	0.1083
12.7 mm.....	½ in. <sup>a</sup>	12.7	0.500	±3	+5	+6	2.67	0.1051
11.2 mm.*....	⅜ in.	11.2	0.438	±3	+5	+6	2.45	0.0965
9.51 mm.....	⅜ in.	9.51	0.375	±3	+5	+6	2.27	0.0894
8.00 mm.*....	⅝ in.	8.00	0.312	±3	+5	+6	2.07	0.0815
6.73 mm.....	.265 in.	6.73	0.265	±3	+5	+6	1.87	0.0736
6.35 mm.....	¼ in. <sup>a</sup>	6.35	0.250	±3	+5	+6	1.82	0.0717
5.66 mm.*....	No. 3½	5.66	0.223	±3	+5	+10	1.68	0.0661
4.76 mm.....	No. 4	4.76	0.187	±3	+5	+10	1.54	0.0606
4.00 mm.*....	No. 5	4.00	0.157	±3	+5	+10	1.37	0.0539
3.36 mm.....	No. 6	3.36	0.132	±3	+5	+10	1.23	0.0484
2.83 mm.*....	No. 7	2.83	0.111	±3	+5	+10	1.10	0.0430
2.38 mm.....	No. 8	2.38	0.0937	±3	+5	+10	1.00	0.0394
2.00 mm.*....	No. 10	2.00	0.0787	±3	+5	+10	0.900	0.0354
1.68 mm.....	No. 12	1.68	0.0661	±3	+5	+10	0.810	0.0319
1.41 mm.*....	No. 14	1.41	0.0555	±3	+5	+10	0.725	0.0285
1.19 mm.....	No. 16	1.19	0.0469	±3	+5	+10	0.650	0.0256
1.00 mm.*....	No. 18	1.00	0.0394	±5	+7½	+15	0.580	0.0228
841 μ.....	No. 20	0.841	0.0331	±5	+7½	+15	0.510	0.0201
707 μ *.....	No. 25	0.707	0.0278	±5	+7½	+15	0.450	0.0177
595 μ.....	No. 30	0.595	0.0234	±5	+7½	+15	0.390	0.0154
500 μ *.....	No. 35	0.500	0.0197	±5	+7½	+15	0.340	0.0134
420 μ.....	No. 40	0.420	0.0165	±5	+12½	+25	0.290	0.0114

NOTE.—Some industries may possibly require more restricted specifications for sieves for special testing purposes.

Attention is called to the Method of Test for Fineness of Hydraulic Cement by the No. 325 Sieve (ASTM Designation C430), which contains requirements for 2-in. diameter sieves used in the mineral industry, especially the cement group, and to the Specification for Precision Micromesh Sieves (ASTM Designation E161), which covers square-hole, electroformed micromesh sieves used mainly as primary reference standards.

**Wire Cloth Sieves. Sieve Cloth. Fixed Ratio Series.**—The openings of the sieve cloth of successive sieves of the standard series progress in the ratio  $\sqrt{2:1}$ , and in selecting sieves from this series, it is customary to take each sieve in a given range, every alternate sieve, or every fourth sieve.

Wire cloth for standard sieves should be woven from brass, bronze, or other suitable wire, should not be coated or plated, and should be plain weave, except that the cloth for sieves for 63  $\mu$  (No. 230) and finer may be twilled weave.

The average opening between the adjacent warp and the adjacent shoot wires, taken separately, should conform to that given in column 3 of Table 31-10, within the "permissible variation in average opening" given in column 5. Column 4 gives the approximate equivalents in inches of the basic values in millimeters given in column 3. The average diameter of the warp and of the shoot wires, taken separately, of the cloth of any sieve should be that given in column 8 of Table 31-10, within the permissible variations given in footnote b of Table 31-10. Column 9 gives the approximate equivalents in inches of the basic values in millimeters given in column 8. The maximum width of individual openings between adjacent warp and shoot wires should not exceed the nominal width of opening by more than the "permissible maximum variation in individual openings" given in column 7 of Table 31-10. An exception may be made, in the case of 8-in. sieves, if the total length of all the portions of rows of openings exceeding this maximum width is less than 4 in. in both the warp and the shoot directions, considered separately, and provided that the sieve is not rejected because of excessive variations in diameter in either warp or shoot wires, or punctures or defects. The permissible variation for not more than 5% of the openings is given in column 6 of Table 31-10.

Both the warp and shoot wires should be crimped in such a manner that they will be rigid when in use.

There should be no punctures or other obvious defects in the cloth.

NOTE.—Until further notice, to permit use of sieves made to the alternate inch openings, a permissible variation in average opening of  $\pm 4\%$  will be allowed for sieves from 26.9 mm. (1.6 in.) to 6.35 mm. ( $\frac{1}{4}$  in.), inclusive.

**Standard 8-in. Sieve Frames. Sieve Frames.**—Frames for all sieves with openings 4.00 mm. or less should be the standard 8-in. size, except for the 3-in. sieves described below. Frames for sieves having nominal openings of less than 25.4 mm. (1 in.) but greater than 4.00 mm. may have frames either of the standard 8-in. size or of larger dimensions as may be specified in individual cases. Frames for sieves having nominal openings of 35.4 mm. (1 in.) or more should be larger than the 8-in. standard.

**Specifications for 8-in. Standard Frames.**—Frames for all sieves with openings 5.66 mm. or less should be the standard 8-in. size, except that frames 3 in. in diameter may be used in the case of sieves 149  $\mu$  (No. 100) and finer, used primarily in the testing of paint pigments. The standard frames should be circular, 8 in.

TABLE 31-10. NOMINAL DIMENSIONS, PERMISSIBLE VARIATIONS, AND  
LIMITS FOR WIRE CLOTH OF STANDARD SIEVES  
[U. S. Standard Series (4th Root of 2 Ratio)]

Sieve Designation		Sieve Opening		Permissible Variations in Average Opening, per cent	Permissible Variation for not more than 5 per cent of Openings, per cent	Permissible Maximum Variation in Individual Openings, per cent	Nominal Wire Diameter <sup>b</sup>	
Standard	Alternate	mm.	in. (ap- proxi- mate equiv- alents)				mm.	in. (ap- proxi- mate equiv- alents)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
107.6 mm.....	4.24 in.	107.6	4.24	±3	+4	+5	6.40	0.2520
101.6 mm.....	4 in. <sup>a</sup>	101.6	4.00	±3	+4	+5	6.30	0.2480
90.5 mm.....	3½ in.	90.5	3.50	±3	+4	+5	6.08	0.2394
76.1 mm.....	3 in.	76.1	3.00	±3	+4	+5	5.80	0.2283
64.0 mm.....	2½ in.	64.0	2.50	±3	+4	+5	5.50	0.2165
53.8 mm.....	2.12 in.	53.8	2.12	±3	+4	+5	5.15	0.2028
50.8 mm.....	2 in. <sup>a</sup>	50.8	2.00	±3	+4	+5	5.05	0.1988
45.3 mm.....	1¾ in.	45.3	1.75	±3	+4	+5	4.85	0.1909
38.1 mm.....	1½ in.	38.1	1.50	±3	+4	+5	4.59	0.1807
32.0 mm.....	1¼ in.	32.0	1.25	±3	+4	+5	4.23	0.1665
26.9 mm.....	1.06 in.	26.9	1.06	±3	+5	+6	3.90	0.1535
25.4 mm.....	1 in. <sup>a</sup>	25.4	1.00	±3	+5	+6	3.80	0.1496
22.6 mm.*....	⅞ in.	22.6	0.875	±3	+5	+6	3.50	0.1378
19.0 mm.....	¾ in.	19.0	0.750	±3	+5	+6	3.30	0.1299
16.0 mm.*....	⅝ in.	16.0	0.625	±3	+5	+6	3.00	0.1181
13.5 mm.....	0.530 in.	13.5	0.530	±3	+5	+6	2.75	0.1083
12.7 mm.....	½ in. <sup>a</sup>	12.7	0.500	±3	+5	+6	2.67	0.1051
11.2 mm.*....	⅞ in.	11.2	0.438	±3	+5	+6	2.45	0.0965
9.51 mm.....	⅜ in.	9.51	0.375	±3	+5	+6	2.27	0.0894
8.00 mm.*....	⅝ in.	8.00	0.312	±3	+5	+6	2.07	0.0815
6.73 mm.....	.265 in.	6.73	0.265	±3	+5	+6	1.87	0.0736
6.35 mm.....	¼ in. <sup>a</sup>	6.35	0.250	±3	+5	+6	1.82	0.0717
5.66 mm.*....	No. 3½	5.66	0.223	±3	+5	+10	1.68	0.0661
4.76 mm.....	No. 4	4.76	0.187	±3	+5	+10	1.54	0.0606
4.00 mm.*....	No. 5	4.00	0.157	±3	+5	+10	1.37	0.0539
3.36 mm.....	No. 6	3.36	0.132	±3	+5	+10	1.23	0.0484
2.83 mm.*....	No. 7	2.83	0.111	±3	+5	+10	1.10	0.0430
2.38 mm.....	No. 8	2.38	0.0937	±3	+5	+10	1.00	0.0394
2.00 mm.*....	No. 10	2.00	0.0787	±3	+5	+10	0.900	0.0354
1.68 mm.....	No. 12	1.68	0.0661	±3	+5	+10	0.810	0.0319
1.41 mm.*....	No. 14	1.41	0.0555	±3	+5	+10	0.725	0.0285
1.19 mm.....	No. 16	1.19	0.0469	±3	+5	+10	0.650	0.0256
1.00 mm.*....	No. 18	1.00	0.0394	±5	+7½	+15	0.580	0.0228
841 μ.....	No. 20	0.841	0.0331	±5	+7½	+15	0.510	0.0201
707 μ*.....	No. 25	0.707	0.0278	±5	+7½	+15	0.450	0.0177
595 μ.....	No. 30	0.595	0.0234	±5	+7½	+15	0.390	0.0154
500 μ*.....	No. 35	0.500	0.0197	±5	+7½	+15	0.340	0.0134
420 μ.....	No. 40	0.420	0.0165	±5	+12½	+25	0.290	0.0114

TABLE 31-10. (Continued)

Sieve Designation		Sieve Opening		Permissible Variations in Average Opening, per cent	Permissible Variation for not more than 5 per cent of Openings, per cent	Permissible Maximum Variation in Individual Openings, per cent	Nominal Wire Diameter <sup>b</sup>	
Standard	Alternate	mm.	in. (approximate equivalents)				mm.	in. (approximate equivalents)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
354 $\mu$ *	No. 45	0.354	0.0139	$\pm 5$	+12 $\frac{1}{2}$	+25	0.247	0.0097
297 $\mu$	No. 50	0.297	0.0117	$\pm 5$	+12 $\frac{1}{2}$	+25	0.215	0.0085
250 $\mu$ *	No. 60	0.250	0.0098	$\pm 5$	+12 $\frac{1}{2}$	+25	0.180	0.0071
210 $\mu$	No. 70	0.210	0.0083	$\pm 5$	+12 $\frac{1}{2}$	+25	0.152	0.0060
177 $\mu$ *	No. 80	0.177	0.0070	$\pm 6$	+20	+40	0.131	0.0052
149 $\mu$	No. 100	0.149	0.0059	$\pm 6$	+20	+40	0.110	0.0043
125 $\mu$ *	No. 120	0.125	0.0049	$\pm 6$	+20	+40	0.091	0.0036
105 $\mu$	No. 140	0.105	0.0041	$\pm 6$	+20	+40	0.076	0.0030
88 $\mu$ *	No. 170	0.088	0.0035	$\pm 6$	+20	+40	0.064	0.0025
74 $\mu$	No. 200	0.074	0.0029	$\pm 7$	+30	+60	0.053	0.0021
63 $\mu$ *	No. 230	0.063	0.0025	$\pm 7$	+30	+60	0.044	0.0017
53 $\mu$	No. 270	0.053	0.0021	$\pm 7$	+30	+60	0.037	0.0015
44 $\mu$ *	No. 325	0.044	0.0017	$\pm 7$	+30	+60	0.030	0.0012
37 $\mu$	No. 400	0.037	0.0015	$\pm 7$	+30	+60	0.025	0.0010

\* These sieves correspond to those proposed as an International (ISO) Standard. It is recommended that wherever possible these sieves be included in all sieve analysis data or reports intended for international publication.

<sup>a</sup> These sieves are not in the fourth root of 2 Series, but they have been included because they are in common usage.

<sup>b</sup> The average diameter of the warp and of the shoot wires, taken separately, of the cloth of any sieve shall not deviate from the nominal values by more than the following:

Sieves coarser than 595 $\mu$ . . . . .	5%
Sieves 595 $\mu$ to 125 $\mu$ . . . . .	10%
Sieves finer than 125 $\mu$ . . . . .	15%

NOTE.—All measurements of openings and wire diameters shall be made on the completed sieve.

(20.32 cm.) in diameter. The height of the sieve from the top of the frame to the cloth should be either about 2 in. (5 cm.), or 1 in. (2.5 cm.). Sieves having a height of 2 in. (5 cm.) should be designated as full-height sieves; those having a height of 1 in. (2.5 cm.) as half-height sieves. The permissible variation on the mean inside diameter  $\frac{3}{16}$  in. below the top of the sieve should be  $\pm \frac{1}{32}$  in. The bottom of the sieve or "sieve skirt" should be so constructed as to have an easy sliding fit in any sieve conforming to the above permissible variations, and in no case should this outside diameter be less than 7.970 in. nor more than 8.000 in. Pans and covers should be so made as to be interchangeable with standard sieves.

*Mounting of Cloth in Frame.*—The cloth should be mounted on the frame with-

out distortion, looseness, or waviness. To prevent the material being sieved from catching in the joint between the cloth and the frame, the joint should be smoothly filled with solder or so made that the material will not catch. The joint or fillet should be so constructed in the 8-in. diameter sieve as to allow a minimum free sieving surface  $7\frac{1}{2}$  in. in diameter.

**Three-Inch Sieves.**—Sieves 3 in. in diameter, used for testing paint pigments, should be made from standard wire cloth 149  $\mu$  (No. 100) or finer. The sieve frames should be circular, about 3 in. (7.6 cm.) in inside diameter, and should not vary from this by more than  $\pm 0.16$  in. (0.4 cm.). The depth of the sieve from the top of the frame to the cloth should be not less than 0.75 in. (1.9 cm.).

The frames should be constructed of first quality sheet brass in such a manner as to be permanently rigid. To prevent the material being sieved from catching in the joint between the cloth and the frame, the joint should be smoothly filled with solder or so made that the material will not catch.

**Miscellaneous Special Sieves.**—The use of special size frames for special purposes is not precluded, as, for example, sieves having a diameter other than 8 in. or the nesting sieves for field use. The use of special size frames should be discouraged where the standard 8-in. frames could be used, because the results are not necessarily comparable.

For some purposes, sieve frames larger than the standard 8-in. diameter may be either square or rectangular instead of circular, and for nominal openings 25.4 mm. (1 in.) and coarser, may be made of metal or hardwood.

**Label Marking.**—Each sieve (except the 3-in. sieve) should bear a label marked with the following information: For sieves 1.00 mm. and coarser, show the sieve designation in millimeters and inches. For sieves finer than 1.00 mm., show the sieve designation in microns and inches. The corresponding U. S. Standard Sieve Number may be added for the convenience of the user.

**Round-Hole Plate Screens (Sieves). Plates.**—Plates used in the manufacture of round-hole screens should be made of brass, bronze, steel, or other rigid material. Thickness of plates should be governed by size of openings as well as screening area of screens and should conform to the requirements prescribed in Table 31-11.

TABLE 31-11.—THICKNESS OF PLATES FOR ROUND-HOLE SCREENS

Screening Area, sq. in.	Diameter of Opening, in.	Thickness of Plate, in.	
		Minimum	Maximum
Under 100	All sizes. . . .	0.049	0.066
100 and over	$\frac{1}{16}$ and $\frac{1}{8}$ . . .	0.049	0.066
	$\frac{1}{2}$ to $2\frac{1}{2}$ , incl.	0.060	0.100
	3 and $3\frac{1}{2}$ . . .	0.075	0.130
	4 and 5. . . .	0.105	0.160
	6 and 8. . . .	0.120	0.175